The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

A Study of the Relationship Between the Dielectric Constant and Accessibility of Cellulose

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June, 1953

A STUDY OF THE RELATIONSHIP BETWEEN THE DIELECTRIC CONSTANT AND ACCESSIBILITY OF CELLULOSE

A thesis submitted by

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for the degree of Doctor of Philosophy
from Lawrence College,
Appleton, Wisconsin

June, 1953

TABLE OF CONTENTS

INTRODUCTION

In recent years the realization has grown that the supermolecular structure of cellulose plays an important role in determining many of the properties of the cellulose. Although the nature of this structure is not readily deduced, indirect methods of study have led to a concept which helps to explain a number of the physical and chemical properties of cellulose. This concept deals with the arrangement of the individual cellulose molecules with respect to each other. Mark (1) gives three arrangements which seem to be particularly characteristic. (1) The amorphous regions are made up of molecular chains arranged completely at random with respect to one another. Such regions are associated with a low specific gravity, and high water adsorption and chemical reactivity, and are responsible for imparting softness and flexibility to the cellulose. (2) Crystalline regions, on the other hand, are built up of molecules arranged in perfect three-dimensional order and impart stiffness and a high Young's modulus to the cellulose. (3) The third region described by Mark is sometimes referred to as the "mesomorphous" or transitional region. This region possesses much of the axial order of the crystalline region but lacts the lateral order. The properties of such a region are intermediate between those of amorphous and crystalline cellulose.

CRYSTALLINE STRUCTURE OF CELLULOSE

Reviews of the development of present concepts of the submicroscopic structure of cellulose have been given by Meyer (2), Sisson (3), and Heuser (4). Verseput (5) has presented a summary of this development which is briefly described here.

In 1858, Nägeli (6) proposed the theory that cellulose was composed of anisotropic crystalline particles, which he named micelles. This theory received little support until the technique for analysis by x-ray diffraction was developed. Confirmation of the presence of micelles was first made by Nishikawa and Ono (7) and later by Scherrer (8). Other workers have carried on this investigation and have deduced the dimensions of the unit cell given in Table I.

TABLE I

DIMENSIONS OF CELLULOSE UNIT CELLS

Axis	Cellulose I (9) (Native)	Cellulose II (10) (Mercerized)
a	8.35 A.	8.1 A.
b	10.30 A.	10.3 A.
c	7.90 A.	9.1 A.
α	84°	62°

In cellulose the unit cell is repeated in all directions to form a crystalline region. Since a cellulose fiber does not consist of a single crystal, this crystalline region cannot extend indefinitely, but is confined to limited regions known as micelles or crystallites. These crystallites have been estimated as being at least 60 to 70 A. wide (at right angles to the fiber axis) and at least 600 A. long (11, 12, 13, 14).

The relationship of these crystallites to the amorphous cellulose in the fiber structure has been the subject of considerable work and theorizing.

The micellar concept embraced a brickwork structure, in which the bricks represent crystallites and the mortar the amorphous material. This theory was useful in explaining the physical and chemical data on cellulose then available.

With the realization that the cellulose molecule is probably ten times as long as the 600 A. estimated for the micelle, the micellar theory was replaced by the continuous structure theory.

The continuous structure theory postulated a continuous, approximately crystalline structure interspersed occasionally by localized disorganization. Certain physical properties of native fibers are explained more satisfactorily by this continuous structure theory; however, the micellar theory offers a better explanation in the case of regenerated materials. Several attempts have been made to form a compromise theory which would fit both circumstances.

The micellar network, or fringe micellar theory may be thought of as such a compromise theory. Sisson describes it as follows (3 p. 219):

> "According to this theory the crystalline areas are not clearly separated from each other by a distinct micellar surface, but rather by an area of partially parallel but disorganized chains. Long crystalline particles are postulated whose outer form is irregular, and defined, especially at the ends, by the projecting, irregularly arranged, primary valence chains which may pass through several micelles and thus tie them together. This gives a net-like structure in which chains occur that are partly crystalline and partly amorphous. Furthermore, it has been proposed that the crystallites are formed as a result of the free rotation of glucose units around their oxygen bridges; crystalline areas result when a group of chains coalesce in a three-dimensional arrangement, while amorphous regions are produced when there is a divergence from the crystalline arrangement. As a consequence cellulose gives a discontinuous crystalline pattern."

Because of the strong intermolecular forces existing in the crystalline regions in such a network structure and the lack of such forces in the amorphous regions, the properties of the cellulose will be greatly affected by the relative amounts of the two regions. This fact has led to extensive investigation of methods for determining the crystalline to amorphous ratio of cellulose.

THE RATIO OF CRYSTALLINE TO AMORPHOUS CELLULOSE

Any attempt to measure the amount of crystalline material in cellulose must take into account the rather vague delimitation of the individual crystallite. No sharp distinction can be made between the crystallite and the amorphous regions, since there must be a certain zone of transition in which the molecular arrangement may vary from nearly perfect order to random disorder. Any quantitative measure of crystallinity will therefore depend upon the method employed and even upon the definition of the terms used.

Both chemical and physical methods are used for estimating the amount of crystalline material in cellulose. The chemical methods of measurement all depend upon the concept of a two-stage reaction. In the first stage the chemicals penetrate readily into the amorphous region of the cellulose where the reaction takes place rapidly. The penetration into the crystallites or micelles takes place much more slowly, only the surface of the micelle being readily available to the chemical action. The rate or extent of chemical reaction is then used to estimate crystallinity. The readily reacting portion of the cellulose (predominantly amorphous cellulose) is often spoken of as the accessible fraction.

Acid hydrolysis, periodate oxidation (15, 16), thallation (17), and formic acid esterification (18) are some of the chemical reactions which have been used to measure crystallinity. Mark (19), using density measurements, found that crystallinity increased during the early stages of acid hydrolysis; and this was later confirmed by the x-ray measurements of Hermans and Weidinger (20). This may account, in part, for the high crystallinity figures obtained by this method compared to measurements made by physical methods.

However, the chemical methods usually give higher values of crystallinity than do the physical methods.

The physical methods of measuring crystallinity depend upon several properties besides accessibility, namely, density (21, 22), x-ray diffraction (23, 24, 25), and the nature of moisture in fibers (26). In addition to these properties, accessibility to deuterium ions (27) and moisture vapor (28, 29) is also used for estimating crystallinity. Verseput (5) has reviewed these various methods of measurements, as well as the theoretical aspects of crystallinity, in some detail; only a brief description of some physical methods of estimating crystallinity will be given here.

Density measurements of cellulose may be related to crystallinity by knowledge of the densities of crystalline and amorphous cellulose (21, 22). The density of crystalline cellulose has been calculated from x-ray data, but that for amorphous cellulose remains in some doubt. Despite the difficulty involved in this method, it appears to give results comparable with other physical methods.

X-ray diffraction photographs may be evaluated quantitatively by determining the visual densities of the films. This evaluation can be broken down into the fraction contributed by each of the cellulose regions (23, 24, 25).

Magne, Portas, and Wakehan (26) calculated from calorimetric measurements the amounts of freezing and nonfreezing water for several fiber to moisture ratios. By making certain assumptions regarding the amount of water associated with amorphous and crystalline celluloses they were able to calculate the amount of noncrystalline cellulose present. Their values for the crystalline

fraction were higher than those obtained by other physical means--closely approaching values obtained by the chemical reaction methods.

Of all of these methods, x-ray measurements probably come closest to being an exact measure of crystallinity; however, x-ray diffraction methods are not capable of detecting the very small crystalline regions. When the reagents and experimental conditions are specified, accessibility measurements are useful on a direct comparison basis with similarly arrived at figures; otherwise these measurements are of little value. One difficulty present in these methods arises from the transition structure existing between completely random orientation and completely crystalline orientation. Such a structure might behave as crystalline material in some types of measurements but would still appear as amorphous cellulose in an x-ray diffraction pattern. Occlusions of amorphous cellulose in crystallites would also give rise to errors in accessibility determinations.

THE DIELECTRIC CONSTANT OF CELLULOSE

When an electrical nonconductor, or dielectric, such as cellulose, is placed between the plates of a charged condenser, a displacement of electrical charges takes place within the dielectric. This displacement of charges is known as polarization and is characteristic of a dielectric under any particular conditions. The polarization gives rise to a field which decreases the effective potential difference between the condenser plates. Since the charge on the condenser plates is constant, this decrease in potential difference results in an increase in the capacitance (ratic of charge to potential difference) of the system. The ratio of the capacitance of a condenser, filled with the dielectric, to its vacuum capacitance is therefore a measure of the polarization of the

dielectric and is commonly called the dielectric constant. When the applied field is alternating, the same relationships hold true. However, the dielectric constant is dependent upon the frequency of the applied field as well as upon temperature and upon the chemical and physical structure of the material.

The displacement of charges, or polarization, takes a number of forms. At frequencies in the visible spectrum, electronic polarizations (displacement of electrons) occur. At frequencies in the infrared range, atomic polarizations take place; and at still lower frequencies dipole polarizations are possible. As a result of the increasing number of types of polarizations possible with decreasing frequency, the magnitude of the dielectric constant increases with a decrease in frequency. Another possible polarization in a heterogeneous material, probably at still lower frequencies, is interfacial polarization, resulting from different electrical properties of the various components. A more complete discussion of these types of polarization and their importance in cellulose has been given by Calkins (30).

By assuming that the molecule is free to rotate and that no interaction between molecules takes place, Debye (31) derived a temperature relationship for dipole polarization which took the form

$$\underline{P} = \underline{A}(\underline{a} + \underline{b} / \underline{T})$$

where $\underline{P}$ is the molar polarization, $\underline{T}$ is the absolute temperature, and $\underline{A}$, $\underline{a}$, and $\underline{b}$ are constants for the particular molecule. His relationship is quantitative for gases and dilute solutions of polar compounds in nonpolar solvents, when his restrictive assumptions are valid; however, this is not the case for the majority of dielectrics.

The Clausius-Mosotti relationship,

$$\underline{P} = [(\varepsilon - 1) / (\varepsilon + 2)] (\underline{M} / \rho),$$

where P is molar polarization, M is molecular weight, ε is dielectric constant, and ρ is density, is similarly based on the assumption of no interaction between molecules. If P is considered constant for a given molecule, the dielectric constant may be related to density by $(\varepsilon - 1)/(\varepsilon + 2)\alpha\rho$. In this form the Clausius-Mosotti equation can often be used even when the basic assumptions for its derivations are not fulfilled by the dielectric under consideration.

In discussing the possible dependence of the dielectric constant of cellulose upon its crystallinity we are primarily interested in the polarizations caused by rotation and vibration of polar groups and portions of molecules. Since a large portion of the dielectric constant of cellulose probably arises from such polarizations, increasing crystallinity, which would decrease this mobility, should cause a decrease in the dielectric constant. Baker and Yager (32) have found this to be true in the case of polydecamethylene sebacamide.

HISTORICAL REVIEW

Reviews of the literature on the dielectric properties of cellulose have been made by Delevanti (33), Hansen (34), Calkins (30), and Verseput (5).

Albert Campbell (35) probably made the earliest dielectric constant measurements on cellulose. For paper samples which had been dried at 110°C. he obtained dielectric constants of 1.7 to 2.6, and for viscose films he obtained values ranging from 6.7 to 7.5 at temperatures from 20 to 70°C.

Stoops (36) investigated the temperature and frequency dependence of the dielectric properties of cellophane. He found that the dielectric constant

increased somewhat with increasing temperature and decreased slightly with increasing frequencies. At 1000 cycles and 25°C. he obtained a value of 7.6. Measurements on cellulose triacetate at these same conditions gave a dielectric constant of 4.0.

The most generally accepted value for the dielectric constant of native cellulose is that obtained by DeLuca, Campbell, and Maass by the method of liquid mixtures (37). They obtained a value of 6.1 for a sample of purified cotton at 25°C.

Shaw and Windle (38) obtained a dielectric constant of 4.04 ± 0.03 for cellophane. A resonant cavity was used with the field parallel to the surface of the cellophane. A frequency of 3000 megacycles was used. The method of desiccation used is not clear.

RELATION TO DENSITY

The validity of the Clausius-Mosotti relationship, relating dielectric constant to density, has been confirmed for several different celluloses. Hansen (34) found it to hold for kraft pulp, Calkins (30) for purified cotton fibers, and Verseput (5) for Cordura viscose rayon fibers. Endicott (39) considered paper as fibrous dielectrics arranged in either series or parallel and found that the series representation fit quite well in the case of a kraft paper.

EFFECT OF MOISTURE

The effect of moisture upon the dielectric constant of cellulose has been investigated extensively. Argue and Maass (40) measured the dielectric constant of cotton at a number of moisture contents and found that the

dielectric constant of the initially adsorbed water was less than one-fourth that of liquid water. They concluded that the first water molecules adsorbed were anchored into fixed positions. The forces holding subsequently adsorbed water molecules gradually diminish until the water molecules reach the state of free water. Garton (41) also concluded that the polarizability of water adsorbed in cellulose was lower than that of free water.

Greenfield (42) measured the dielectric constant of kraft paper at a series of vacuums, which have been shown to be equivalent to a series of relative humidities (30). Reduction of the pressure from 400 to 0.25 mm. caused a decrease in the power factor of 80% but resulted in a decrease in the dielectric constant of only 3%. Calkins (30) found that the dielectric constant of cellulose was virtually independent of small amounts of adsorbed water.

EFFECT OF CRYSTALLINITY

Calkins (30) found that the dielectric constant of fibrous regenerated cellulose was considerably higher than that of native cellulose or even cellophane. Pressing of the regenerated cellulose caused a decrease in its dielectric constant accompanied by a similar decrease in its moisture regain, indicating a possible relationship between dielectric constant and crystallinity.

Dakin (43) measured the dielectric constant of several celluloses by the method of liquid mixtures. He obtained variation in dielectric constants which were in general accord with x-ray determination of crystallinity on similar celluloses.

Verseput (5) investigated the relationship between dielectric constant and crystallinity in greater detail, calculating accessibilities from a number of moisture regain values. His method of measurement of dielectric constant involved compressing the cellulose samples at high pressure to decrease the void volume in the condenser. A wide variation in the apparent densities of the samples necessitated the use of the Clausius-Mosotti relationship to compare the dielectric constants at the same apparent density. Although the correlation between dielectric constant and accessibility found by Verseput was quite good, certain anomalies led him to conclude that "An interpretation of dielectric constant as a measure of crystallinity must be different from that placed on existing methods."

PRESENTATION OF THE PROBLEM

Two possible sources of difficulty were present in Verseput's work. First, the use of high compacting pressure on cellulose is known to cause changes in its dielectric constant (5, 30); and second, the validity of the relationship between dielectric constant and density, derived from the Clausius-Mosotti relationship, has not been established for all celluloses nor for extrapolation to high density.

The purpose of this problem is to determine the dielectric constants of celluloses at or near their ultimate density by the method of DeLuca, Campbell, and Maass, and to examine the relationship existing between such values and accessibility. This method of dielectric constant measurement is free from any discrepancies introduced by correcting dielectric constants for density variations or by subjecting the cellulose to high pressure.

The celluloses to be examined will be selected with the purpose of extending the accessibility range examined by Verseput.

In addition to the accessibility study, an examination of the effects of inter- and intrafiber bonds upon the dielectric constant of cellulose will be made.

The acconplishment of these aims involves the development of suitable apparatus and techniques and the modification of existing apparatus for the measurement of dielectric constant.

EXPERIMENTAL

THEORY OF LIQUID IMMERSION METHOD FOR MEASURING DIELECTRIC CONSTANT

Argue and Maass (40), in their work on the dielectric constant of water adsorbed on cellulose, have shown how the apparent dielectric constant of cellulose can be determined by the orientation of the fibers with respect to the condenser plates. If all of the fibers were to lie parallel to the plates, the dielectric constant of the system would by given by

$$\varepsilon_m = 1 / [(\underline{v}_c / \underline{V}\varepsilon_c) + (\underline{V}_r / \underline{V}\varepsilon_r)]$$

where

$\underline{v}_c / \underline{V}$ is the volume fraction of cellulose.

ε_c is the dielectric constant of the cellulose.

$\underline{v}_r / \underline{V}$ is the volume fraction not occupied by cellulose.

ε_r is the dielectric constant of material filling the space represented by $\underline{v}_r / \underline{V}$.

ε_m is the dielectric constant obtained by capacitance measurements.

If all of the fibers are perpendicular to the plates, extending from one plate to the other, the dielectric constant would be given by

$$\varepsilon_m = (\underline{v}_c \varepsilon_c / \underline{V}) + (\underline{V}_r \varepsilon_r / \underline{V})$$

DeLuca, Campbell, and Maass (37) utilized the fact that when ε_r is made equal to ε_c, the apparent dielectric constant, ε_m, is equal to the dielectric constant of the cellulose, ε_c, regardless of fiber orientation. In their work, the capacitance of a condenser filled with various concentrations of ethylene chloride in benzene was plotted as a function of the concentration. This capacitance-concentration curve was obtained in a second run with the

condenser packed with cellulose. The intersection of the two curves was at a capacitance equivalent to a dielectric constant of 6.1. This figure was confirmed by surrounding the cellulose with a liquid of dielectric constant 6.1. Complete penetration of the liquid into the cellulose was obtained by adding the liquid when the system was evacuated and then raising the pressure to atmospheric.

When the dielectric constants of the liquid and of the liquid-cellulose mixture are obtained with the same filling operation, an accurate knowledge of the liquid concentration is not critical; and the possibility of a change in concentration in the filling operation is of no importance. In this case the dielectric constant of the liquid-cellulose mixture (ε_m) can be plotted as a function of the dielectric constant of the liquid (ε_r), and the point on this curve at which $\varepsilon_m = \varepsilon_r$ determines the dielectric constant of the cellulose. This method is illustrated in Figure 1.

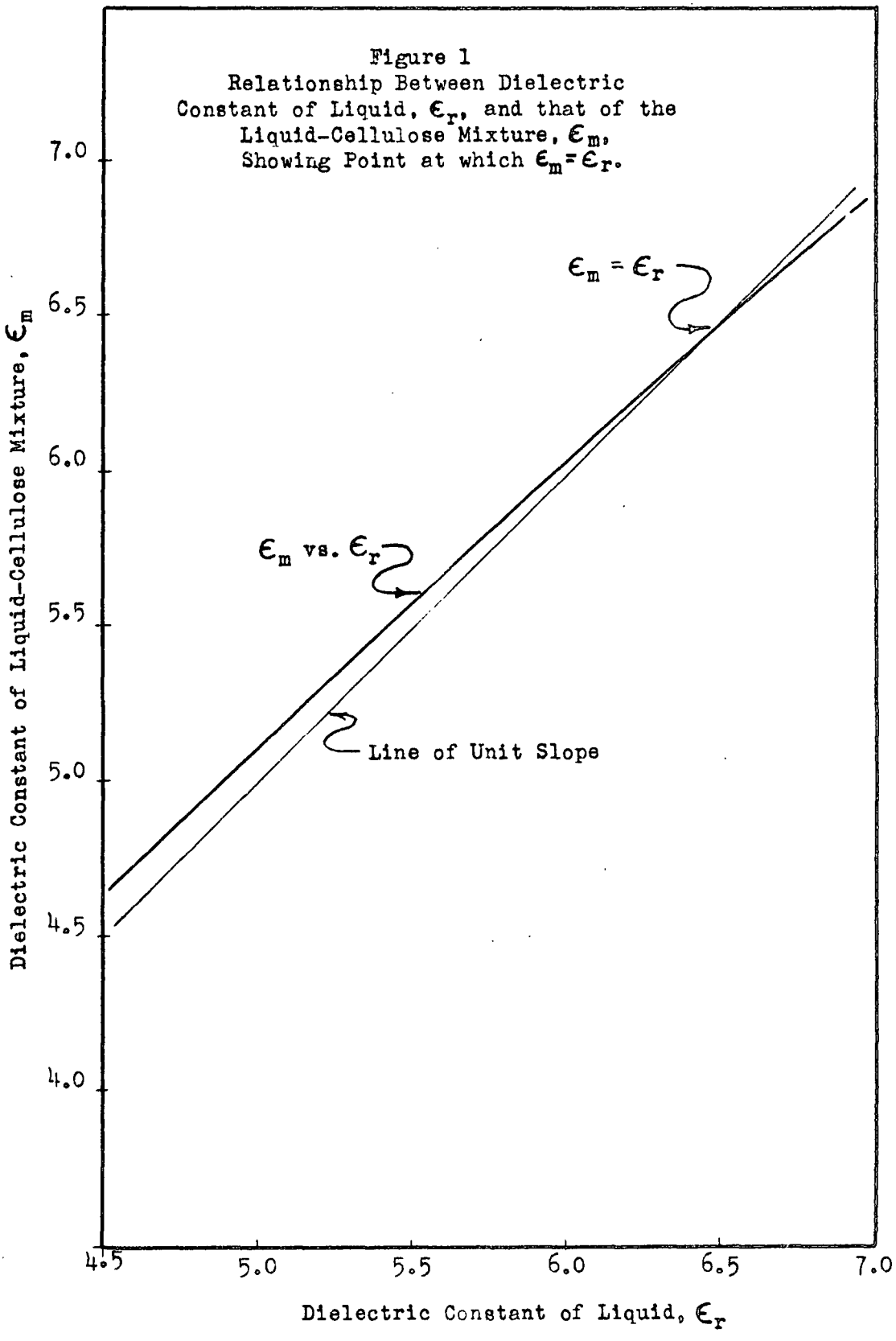
Using this method, several points must be obtained near the intersection before the intersection can be determined accurately. It is desirable that the intersection be predicted from fewer measurements.

Lichteneker (44) carried out some experiments on the dielectric constant of small particles suspended in liquids and found that the Maxwell-Rayleigh rule of mixtures was valid for such a system. His results showed that

$$\log \varepsilon_m = [(\underline{v}_c \log \varepsilon_c) / \underline{V}] + [(\underline{v}_r \log \varepsilon_r) / \underline{V}]$$

Argue and Maass (40), in their measurements of the dielectric constant of water adsorbed on cellulose, used the equation for fibers lying perpendicular to the condenser plates. The assumption made in writing this equation, however, appears to have less chance for validity in the case of cellulose

Figure 1
Relationship Between Dielectric Constant of Liquid, ϵ_r, and that of the Liquid-Cellulose Mixture, ϵ_m, Showing Point at which $\epsilon_m = \epsilon_r$.



pads than the equation for fibers parallel to the plates.

In the present work both of the above equations were found to have some utility in predicting intersections of the aforementioned curves; however, the range of their usefulness did not extend over the entire dielectric constant range. The logarithmic rule was applicable only when at least one of the liquids measured had a dielectric constant within 0.2 of the dielectric constant of the cellulose.

The dielectric constant of ethylene chloride is very dependent upon temperature. In the range of 20 to 40°C. this temperature dependence can be represented by $\underline{d} \log \varepsilon / \underline{dt} = 0.0024$ (55). The temperature coefficient for mixtures of ethylene chloride and benzene is considerably less, since for benzene $\underline{d} \varepsilon / \underline{dt} = -0.002$ (55) in this temperature range. Since the dielectric constant of cellulose has a slight positive temperature coefficient, the variation of temperature provides a means for continuously varying the dielectric constant of the reference liquid with respect to the dielectric constant of the cellulose. If the dielectric constants of the liquid and of the liquid-cellulose mixture are each plotted as a function of temperature, the slope of the liquid-cellulose curve is somewhat less than the slope of the liquid curve. Over small temperature ranges both of these curves can be represented by straight lines, the intersection of which (i.e., $\varepsilon_m = \varepsilon_r$) indicates the dielectric constant of the cellulose at the corresponding temperature. When curves for two liquids are obtained, a line connecting the two intersections obtained indicates the dielectric constant of cellulose as a function of temperature. For the small temperature ranges investigated, all of these curves can be represented by straight lines. This method of determining the dielectric constant is illustrated in Figure 2.

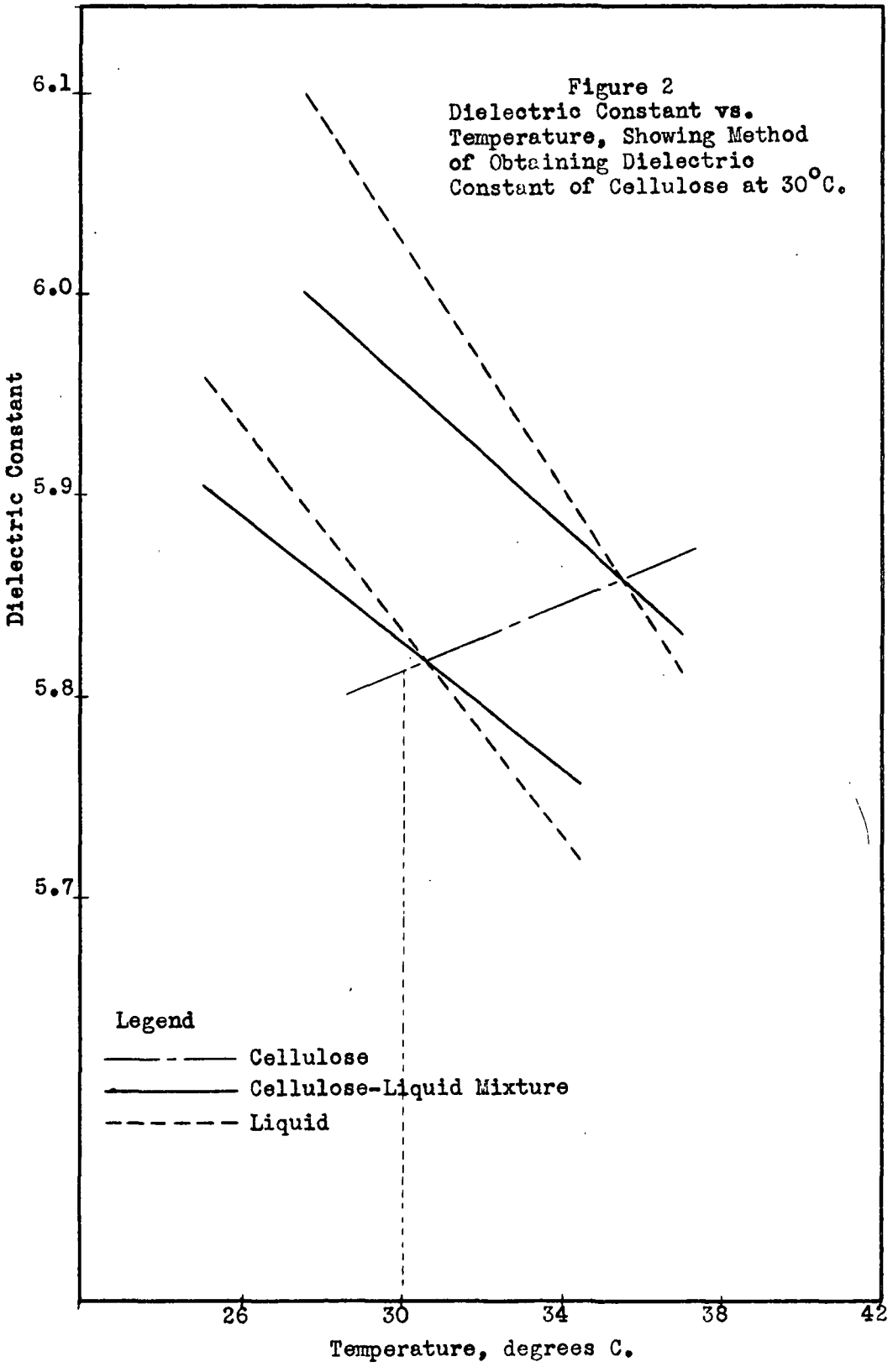


Figure 2
Dielectric Constant vs. Temperature, Showing Method of Obtaining Dielectric Constant of Cellulose at 30°C.

This temperature variation method was used in the bonding and crystallinity studies. Preliminary work was done at one temperature, 30°C., with the intersections being determined by one of the previously mentioned methods.

APPARATUS FOR THE MEASUREMENT OF DIELECTRIC CONSTANT

CAPACITANCE BRIDGE

The modified conjugate Schering capacitance bridge used in the present work was built and described by Delevanti (33). Certain modifications of the circuit, however, were found necessary for the present work. The modified bridge circuit is shown in Figure 3. In this figure the following symbols are used:

C_1 - General Radio variable air capacitor, type 246-V, 1500-mmfd.

C_2 - General Radio precision capacitor, type 722-D, 25-110-mmfd., or 100-1100-mmfd.

C_3 and C_4 - 100-mmfd. air capacitors.

C_5 and C_6 - 400-mmfd. air capacitors.

R_1 and R_2 - 10-megohm rheostats with 1000-megohm cellophane run-offs.

R_3, R_4, R_5, and R_6 - 10,000-ohm precision-matched noninductive resistors.

R_7 - 100-ohm rheostat

R_8 - 25-ohm potentiometer rheostat

D - Detector, a high-amplification vacuum-tube amplifier [described in detail by Verseput (5)].

C_p, C_r - Test condenser or control condenser.

S_1, S_2 - Shielded switches.

The entire bridge is shielded by copper housing, and the external leads are shielded cable.

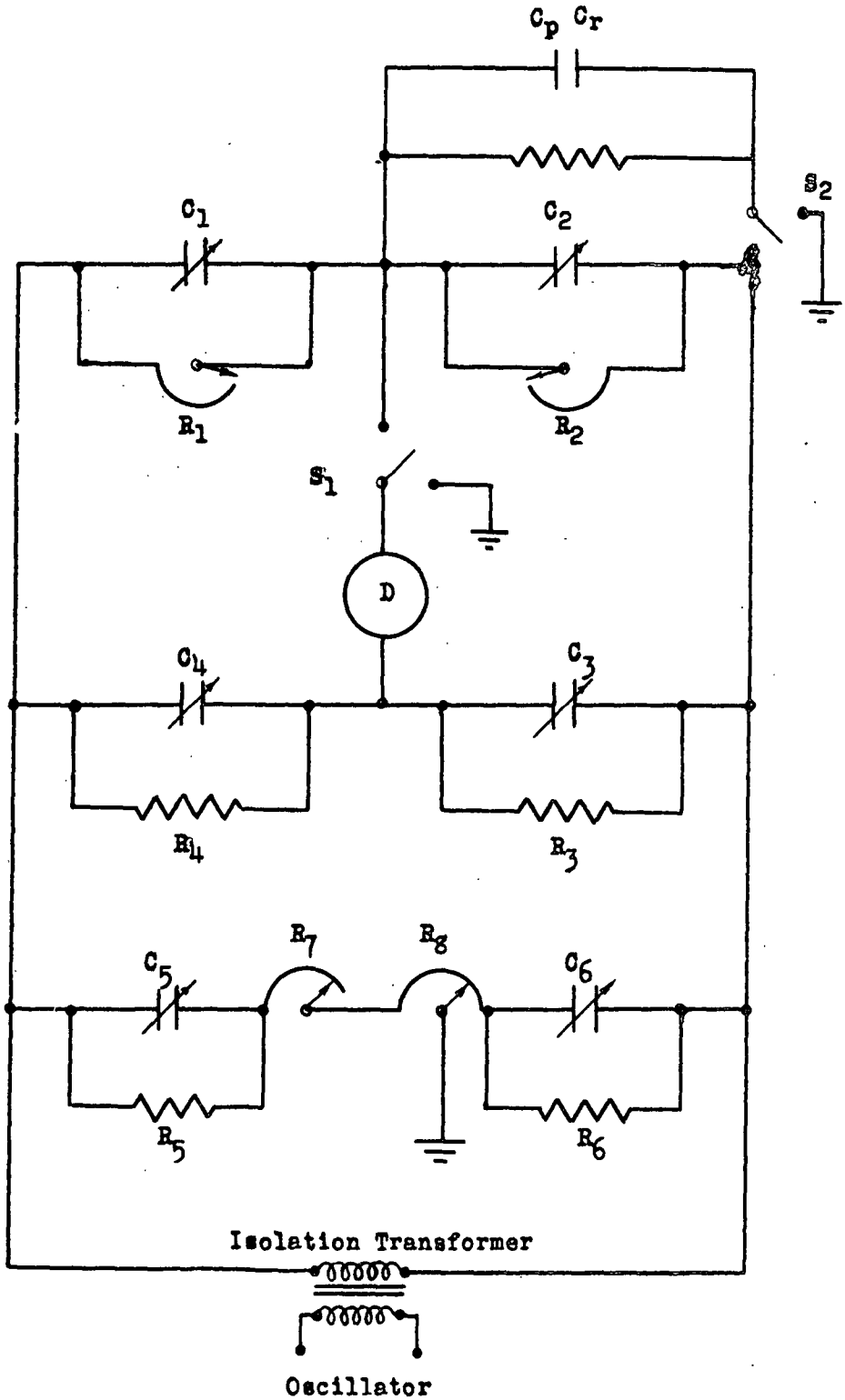


Figure 3
Electrical Circuit of Schering Bridge

SOURCE OF ALTERNATING VOLTAGE

The transitron-type oscillator built and described by Hansen (34) was used as a source of alternating voltage for the Schering bridge. This oscillator is capable of producing a sinusoidal alternating voltage ranging in frequency from 200 to 10,000 cycles per second. Because the wave form varied considerably with amplitude, an oscilloscope was used to monitor the output. The oscillator was permanently set at 10,000 cylces, since a loss of sensitivity resulted at lower frequencies.

TEST CAPACITOR SYSTEM

The test capacitor system (Figure 4) was designed to allow capicatance measurements on a condenser containing both the cellulose sample and reference liquid and on a condenser containing the reference liquid alone. The center plate is common to both condensers and its lead to the bridge includes the switch S_2 shown in Figure 3. Both the center plate and the lower plate are made of one-eighth inch brass to minimize any deformation caused by the insertion of the sample. This condenser is designated C_p. The upper plate is one-sixteenth inch brass and forms the second condenser, C_r, with the center plate. This condenser is used only with the reference liquid. The supports for the condenser plates are made of three-eighths inch Teflon rod. The lower end of each support was machined to fit the corresponding socket in the lower half of the condenser housing. The upper portion was machined to a diameter slightly over one-eighth inch and threaded for the entire length of the one-eighth inch section. A brass nut was then screwed down until it rested firmly against the Teflon shoulder.

Glass washers were cut from six millimeter glass tubing and ground to uniform thickness (approximately 0.05 inch) for use as spacers. The condenser

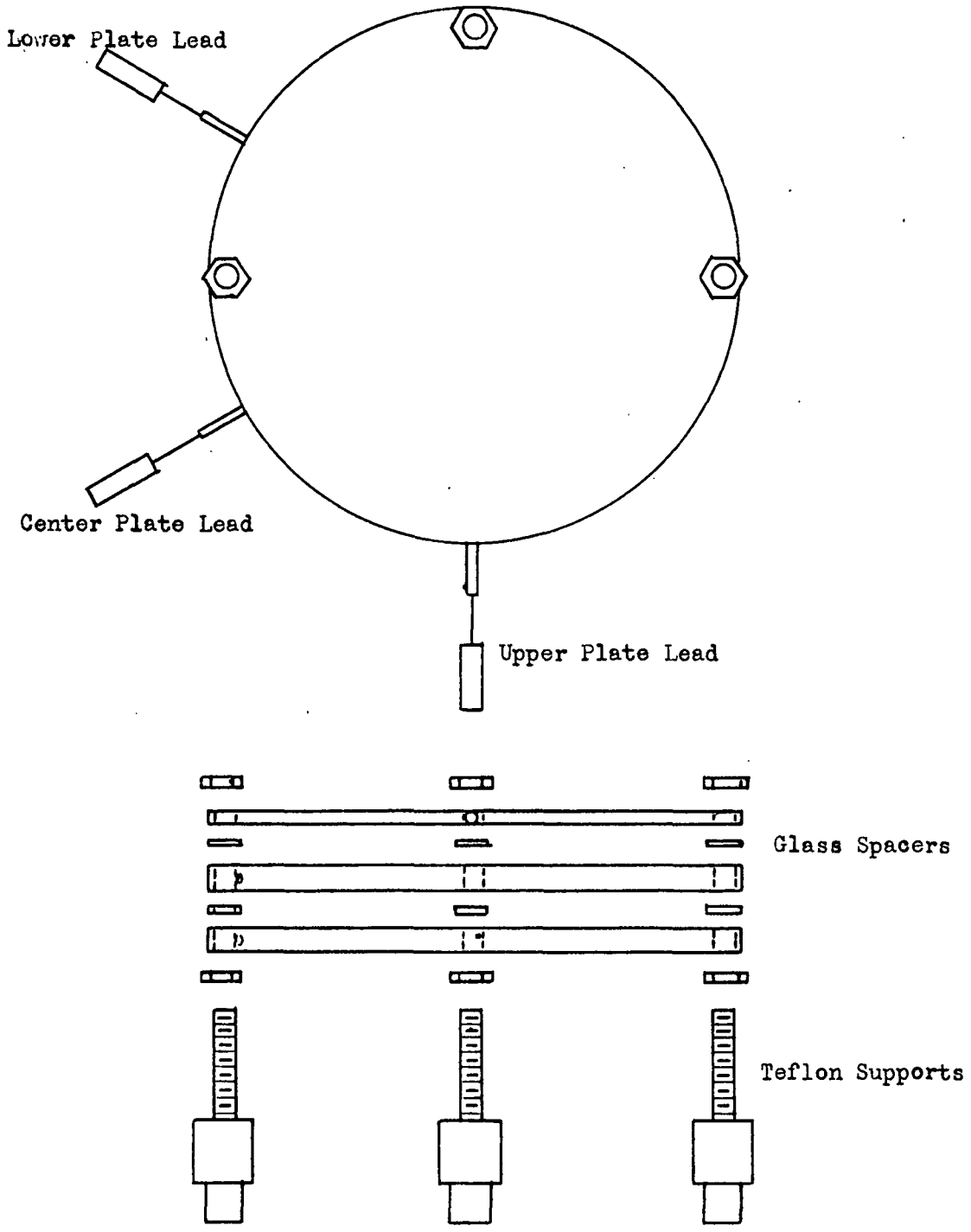


Figure 4
Test Condensers

plates were drilled for three supports placed to leave one side completely open so that the sample could be inserted without dismantling the condenser. The plates were held in place by brass nuts on the Teflon supports. The plates, spacers, and nuts fit very snugly on the oversize Teflon supports.

The cell for housing the condenser was machined from a six-inch round brass rod. Its construction is shown in Figure 5. Teflon gaskets are used to insure a vacuum-tight fit and to insulate the condenser leads from the housing. The gaskets were cut so that their outer edge has slightly less thickness than the inner edge. The condenser leads are brought out between the two gaskets. The Teflon gaskets could be drawn down sufficiently to form a seal around the leads.

The three condenser leads were brought out at intervals of 60° to reduce lead capacitance. In the interior of the cell these leads were made of one-sixteenth inch brass rod. Imbedded in the gaskets at their outer edge are the copper sockets into which the external leads are plugged. The copper sockets are connected to the interior leads by short lengths of soft iron wire. The vacuum seal is obtained by drawing the gaskets down upon this iron wire. The external leads are conducted through the constant temperature bath in three-eighths inch copper tubing which is attached to the brass housing by flanges.

The shielded switch, S_2 in Figure 3 is attached at the top of the copper tube enclosing the lead from the center condenser plate. A cable connector is attached to the switch housing. This connector is necessary in order to keep the condenser plate, which is not connected to the bridge, at the same potential as the center plate. The equivalent circuit is shown in Figure 6.

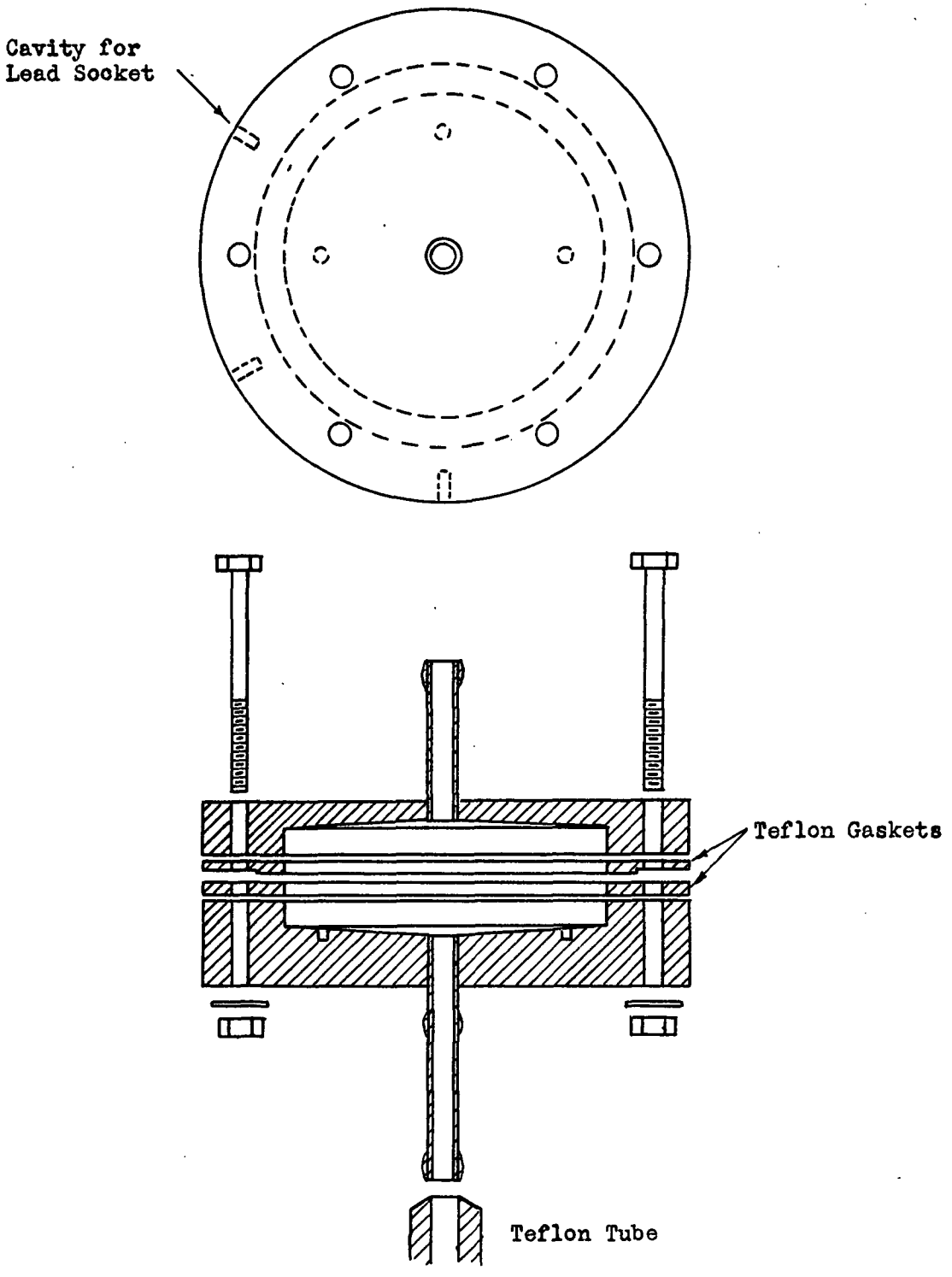
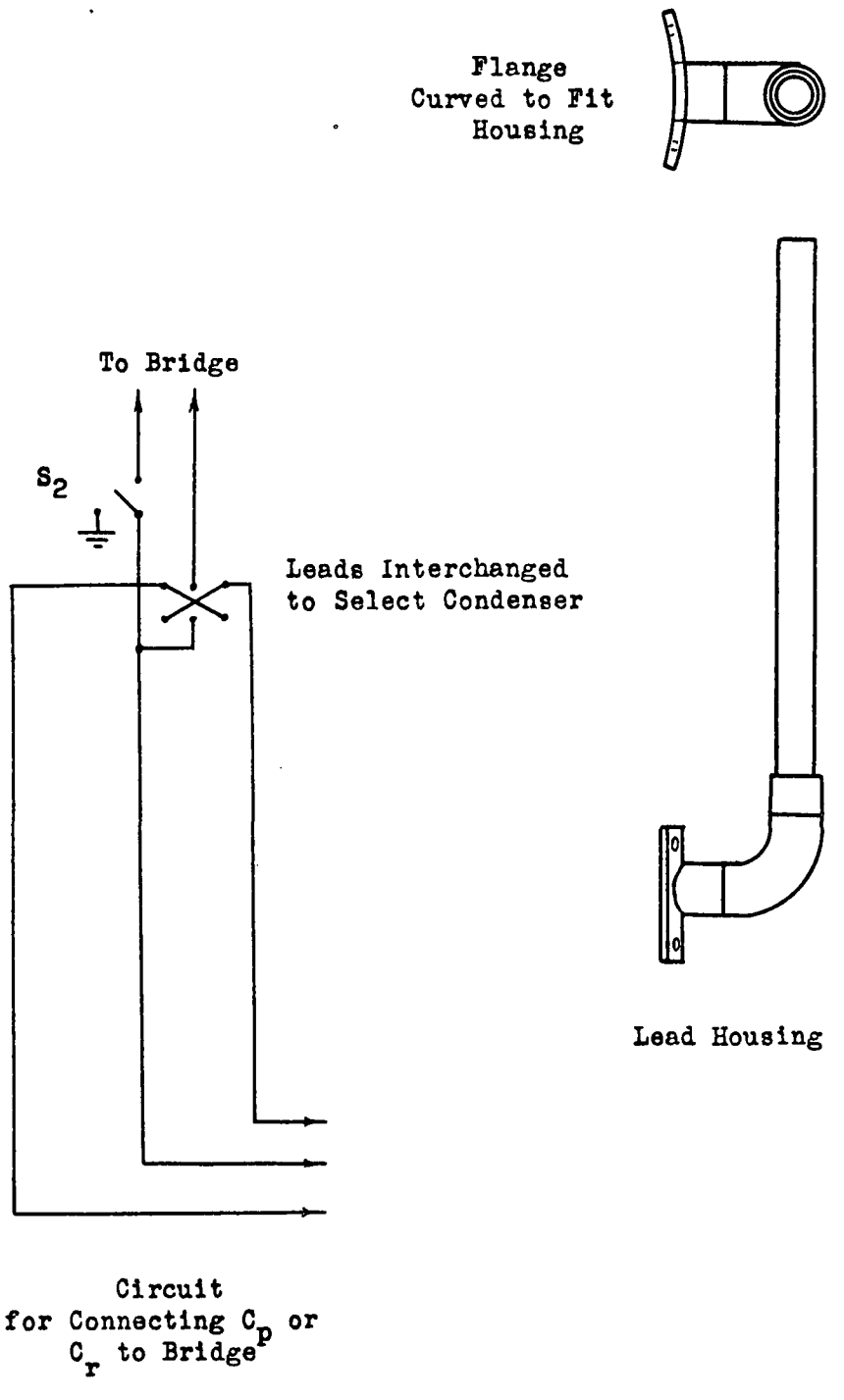


Figure 5
Test Condenser Housing



Circuit
for Connecting C_p or
C_r to Bridge

Figure 6

VACUUM SYSTEM

The vacuum system is shown in Figure 7. The condenser housing may be removed by disconnecting the dry ice trap at X and sliding the copper tube of the housing out of the Teflon tube. Teflon or glass tubing is used to connect all parts of the system which normally come into contact with the reference liquids. The remainder of the system is connected with rubber tubing.

A rubber gasket on the bottom of the housing butts against the top of the Teflon tubing and against a rubber sleeve over the Teflon. Rubber cement is used to insure a tight fit at this point. The rubber is sufficiently isolated from the main channel of the solvents by the long copper tube so that no contamination results. The Teflon is joined at the top of the housing in the same manner as below, except that a permanent joint has been formed by shrinking the Teflon onto the copper.

Joining the Teflon to the glass was accomplished by forming a bulge near the end of the glass tubing of slightly greater diameter than the inside diameter of the Teflon tubing, and then forcing the enlarged glass tubing inside the heat softened Teflon. When the Teflon cooled, the joint was wrapped with rubber tape to restrict the movement of the glass and insure a vacuum tight joint. No difficulty was encountered with the liquids attacking the rubber when these joints were properly made.

As can be seen from Figure 7, two stopcocks are used which contact the reference liquid before the liquid can enter the condenser chamber. The stopcock grease for use on these stopcocks was made up of a mixture of glycerin, dextrin, and mannitol (45). The mixture was boiled for a few minutes and then allowed to cool. This lubricant was not attached by either of the

1-Phosphorous Pentoxide Drying Tube
2-Sulfuric Acid Gas Drying Bottles
3 and 3'- Vacuum Flasks
4-Dry Ice-Acetone Traps
5-Filling Chamber
6-Storage Bottle
7-Condenser Housing
8-Drain

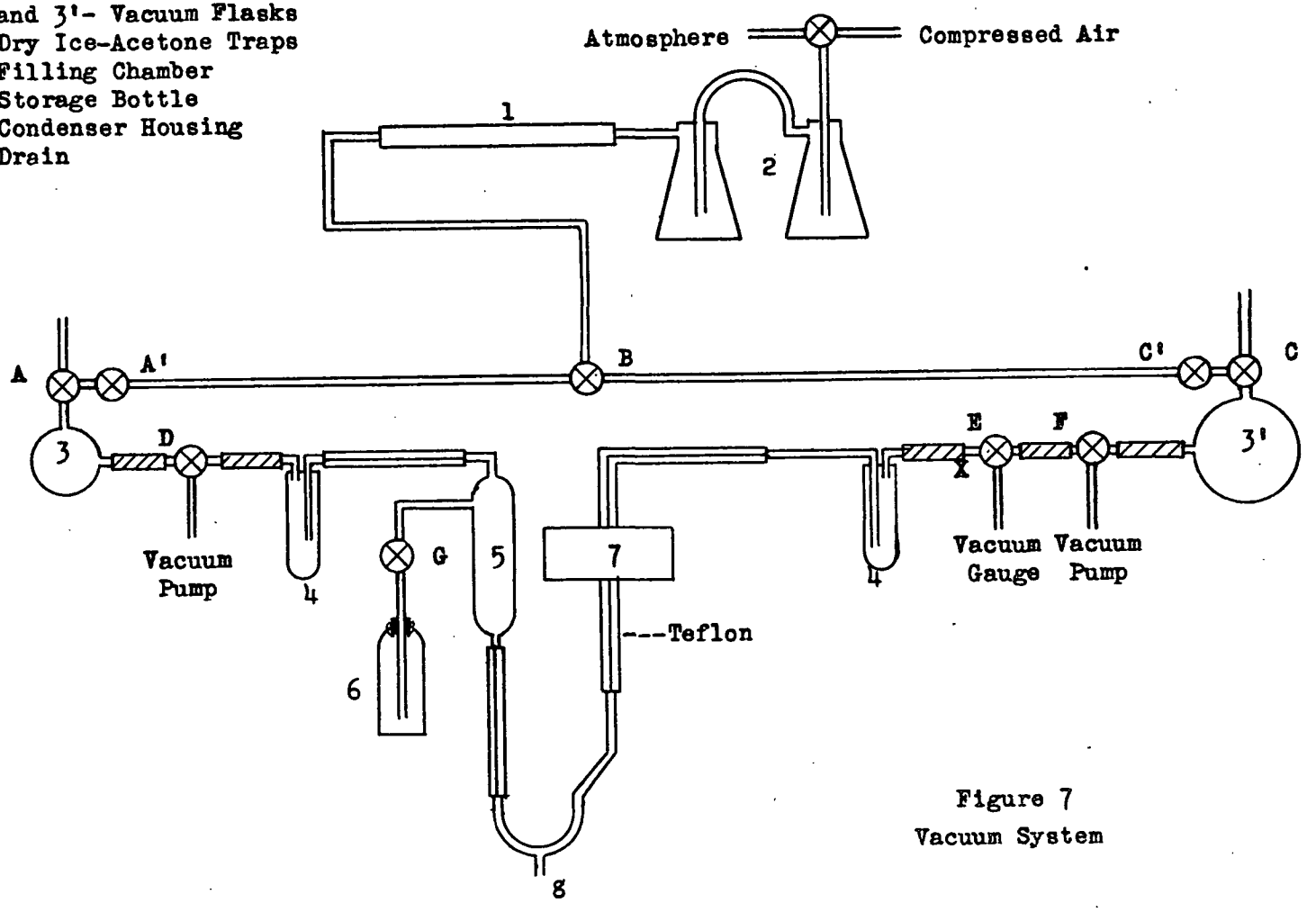


Figure 7
Vacuum System

liquids, nor was the liquid contaminated (as determined by conductivity measurements).

Cellulose samples subjected to prolonged evacuation and several liquid changes underwent no change in dielectric constant, indicating that contamination of the cellulose by constituents of the stopcock lubricant was negligible.

CELLULOSE SAMPLES FOR DIELECTRIC CONSTANT MEASUREMENTS

DESCRIPTION OF PULPS

For all preliminary work and for the study on bonding, a highly beaten cotton linters pulp was used. Analysis of the linters showed 98.5% alpha-cellulose, 0.06% ash; and 4.1% extractable by hot 5% caustic soda solution (46). A portion of the linters was beaten in a Valley laboratory beater for one hour and forty-five minutes to a freeness of 290-cc. Schopper-Riegler. This pulp was stored at beater consistency (2%) at room temperature in a 0.5% formaldehyde solution. Verseput (5) found that storage in formaldehyde did not cause a significant change in the dielectric constant of cellulose. This pulp was used in the development of techniques in sample preparation and dielectric constant measurements.

A second portion of the linters was beaten to a freeness of 290-cc. Schopper-Riegler and stored at beater consistency in a 0.5% formaldehyde solution at 47°F. This pulp was used for bonding studies and in the crystallinity study.

A portion of the beaten cotton linters was hydrolyzed in boiling 2.5 N hydrochloric acid for fifteen minutes to produce a hydrocellulose according to the method of Battista (47). The hydrocellulose was washed thoroughly with distilled water and dilute ammonium hydroxide until the wash water was neutral. Samples of this pulp dried from water produced a hard, brittle

sheet. When dried by solvent replacement the product was a very white powder.

Two regenerated celluloses were used in the crystallinity study. One was a sample of unplasticized cellophane obtained from the E. I. du Pont de Nemours & Company, Inc. The second was a sample of regenerated viscose prepared by the cellulose department at The Institute of Paper Chemistry. This material was regenerated without any tension being applied to the filament. This regeneration procedure yielded a coarse product which was a mixture of filamentous and filmlike cellulose. The product was disintegrated in a Waring blender and washed thoroughly before storing in formaldehyde at 47°F.

A Brown Company softwood alpha pulp and a Weyerhaeuser bleached sulfite pulp were used without any treatment other than brief disintegration in a Waring blender. Analysis of the alpha pulp showed 0.0% lignin, 3.1% pentosans and 90.2% alpha. Analysis of the sulfite pulp showed 0.1% lignin, 2.6% pentosans, and 86.4% alpha-cellulose (48).

PREPARATION OF SAMPLES

Samples were prepared in a nine-centimeter Büchner funnel on a porous, acid-washed, filter paper. The pulp was washed three times in distilled water with dewatering between washes. Approximately two grams of the pulp were used for each sample. When the pad was formed it was placed between two circles of filter paper and pressed between blotters at fifty pounds per square inch for thirty seconds. Water-formed sheets (samples B through G) were dried in drying rings to prevent curling. The samples were cut to the proper size after drying. Pulp samples for the crystallinity study were swollen in cold water (47°F.), drained, and washed three times with absolute methanol. They were then stored in methanol for two weeks. The methanol was

replaced with sodium-dried ether, and the ether with sodium-dried benzene. Three washes in the latter two solvents were used. After each washing, the solvent was drained off in a Büchner funnel without, however, permitting air to be drawn through the pad. Approximately 100 cc. of solvent per gram of pulp per wash were used. The pulps were stored in benzene until needed. The sample pads for dielectric constant measurements were formed from the benzene suspension, pressed at 50 p.s.i. for 30 seconds, and cut to the proper size. The pressing was required to reduce the thickness of the pad to a point where it could slip easily into the test capicitor.

TABLE II

CELLULOSES USED FOR DIELECTRIC CONSTANT DETERMINATIONS

Sample Designation	Cellulose	Use
B	Beaten cotton linters	Bonding study
C	Beaten cotton linters	Bonding study
D	Beaten cotton linters	Bonding study
E	Beaten cotton linters	Bonding study
E'	Beaten cotton linters	Bonding study
F	Beaten cotton linters	Bonding study
G	Beaten cotton linters	Bonding study
J	Beaten cotton linters	Crystallinity study
K	Hydrocellulose	Crystallinity study
L	Cellophane	Crystallinity study
M	Unstretched regenerated viscose	Crystallinity study
N	Wood alpha	Crystallinity study
P	Bleached sulfite	Crystallinity study

The cellophane samples were cut to the proper size before swelling in water. The solvent treatment was the same as for the pulps. Ten thicknesses, approximately two grams, were used for each sample.

CHANGES IN FREENESS OF PULP

The beaten cotton linters used in the preliminary work was stored at beater consistency at room temperature. Over a six-month period the freeness of this pulp increased from 290 cc. to 375 cc. Schopper-Riegler. The drainage time of the aged pulp, as measured in the British sheet mold, was thirteen seconds for a one-gram sample. A second batch of the same cotton linters, beaten to a freeness of 290 cc. Schopper-Riegler, had a drainage time of sixty-nine seconds when freshly beaten. After storage for three months at 47°F., the drainage time and freeness of this pulp remained unchanged.

The increase in freeness of the pulp stored at room temperature could not be attributed to microbiological attack. Plate-outs on nutrient agar gave a count of only four colonies per cubic centimeter.

Jayme and Rothamal (54) found that the swelling of a pulp showed a significant decrease when the temperature was raised from 2 to 28°C. The time allowed for this change was two hours. It appears possible that the change in freeness noted above could be attributed to slight thermal effects over extended periods of time.

Although these freeness changes were originally believed to alter the dielectric constant, later work indicated that this was not the case.

Nevertheless all pulps used in the bonding and crystallinity studies were stored at low consistency at 47°F. until immediately prior to their use. As noted above, this method of storage was not accompanied by a significant change in the freeness of the pulp.

DENSITY DETERMINATION

Davidson (49) has measured the specific volume of cotton with three different media: gaseous helium, liquid toluene, and liquid water. His results show that whereas the helium and toluene give comparable results of about 0.64 cc. per gram, the specific volume in water is about 0.62 cc. per gram. Campbell and Russell (50) found a specific volume of 0.62 for cellulose which had been swollen in water, then soaked successively in acetone and benzene.

Since all dielectric constant measurements for correlation with accessibility were made on solvent replacement-dried samples, no density corrections should be necessary. However, density measurements were desirable for the comparison of the dielectric constants of bonded and unbonded cellulose. The density of unbonded (solvent replacement-dried) cellulose is of interest in determining how closely the actual density approaches the ultimate density.

The apparatus for density determinations consisted of a vacuum desiccator fitted as shown in Figure 8. This system allows the cellulose to be vacuum dried with dry air flushing and finally for the cellulose samples to be immersed in a suitable buoyancy liquid while the system is evacuated.

Density determinations were made on water-dried cellulose, on solvent replacement-dried cellulose which had not contacted moisture after the solvent

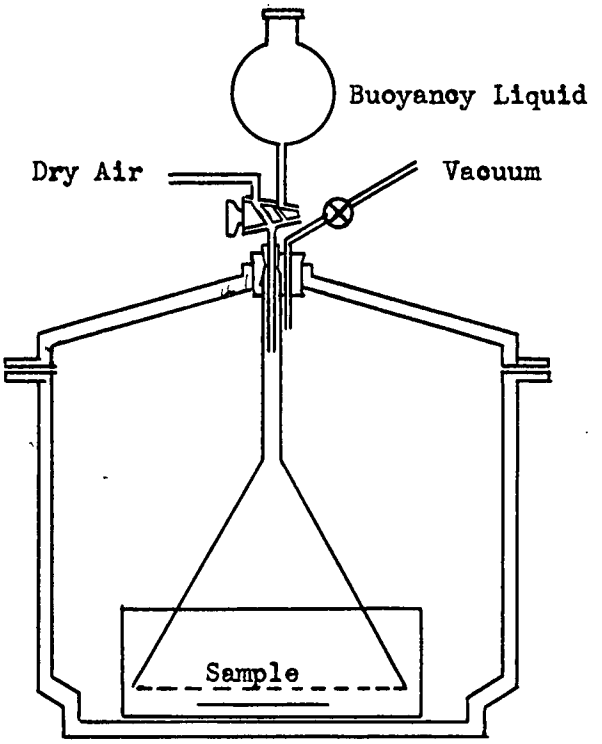


Figure 8
Density Determination Apparatus

replacement treatment, and on solvent replacement-dried cellulose which had been exposed to the atmosphere. Sample weights were approximately one gram. When the samples were immersed and the pressure raised to atmospheric, the liquid temperature was raised to 73°F. The immersed samples were weighed on a metal frame which was suspended from the balance by a fine wire. The weight of the immersed frame was determined with the liquid at the same point on the suspension wire. The entire operation was then repeated with a second buoyancy liquid and the density of the cellulose calculated from

$$\rho_c = [\underline{W}_1 (\rho_2 - \rho_1) / (\underline{W}_1 - \underline{W}_2)] + \rho.$$

where

ρ_c = density of cellulose

$\underline{W}_1$ = weight of cellulose in liquid No. 1

$\underline{W}_2$ = weight of cellulose in liquid No. 2

ρ_1 = density of liquid No. 1

ρ_2 = density of liquid No. 2

The buoyancy liquids used were benzene and ethylene chloride. All cellulose samples were beaten cotton linters.

TABLE III

DENSITY MEASUREMENTS

Water-dried cellulose	1.529 g./cc.
Solvent replacement-dried cellulose	1.581 g./cc.
Solvent replacement-dried cellulose, after exposure to atmosphere	1.545 g./cc.

The density of crystalline cellulose, as calculated by Lyons (51) from unit cell dimensions, is 1.582. The solvent replacement technique of

drying thus appears to produce a cellulose of a density very close to that of crystalline cellulose. Exposure to water vapor evidently collapses portions of the expanded capillaries which remain as a result of solvent replacement drying. This collapse was suggested by Haselton (52) to explain the decrease in specific surface of cellulose similarly treated.

ACCESSIBILITY DETERMINATION

WATER-VAPOR ADSORPTION

The Wink (53) method was used to determine the moisture regain of the cellulose samples for three relative humidities at 73°.

The Wink apparatus consists of a covered crystallizing dish in which is suspended an open Petri dish holding the sample. The Petri dish, plus sample, is weighed without removal from the crystallizing dish by means of a brass rod which passes through a hole in the cover. This hole is normally closed by a conical brass collar around the brass rod. This mechanism serves to hold the Petri dish above the bottom of the crystallizing dish which is covered with a saturated solution of the desired salt. The sample is weighed periodically until equilibrium is reached.

The salt solutions used in this work and the respective relative humidities are shown in Table IV.

TABLE IV

RELATIVE HUMIDITIES ABOVE SATURATED SALT SOLUTIONS (5)

Lithium chloride	11.1%
Magnesium chloride	32.9%
Sodium nitrite	64.8%

All samples were dried with phosphorus pentoxide before placing over the salt solutions. When moisture equilibrium was reached the samples were oven dried at 105°C. to obtain the dry weight of the sample. Although this method of drying may not be complete, the results so obtained should be comparable. Duplicate runs were made at each relative humidity.

ACCESSIBILITY CALCULATIONS

Accessibilities were calculated according to the isotherm of Hailwood and Horrobin (29). This isotherm is based upon the assumption of an ideal solid solution of unhydrated cellulose, hydrated cellulose, and dissolved water. Only the monohydrate is assumed in calculations and good agreement has been obtained between calculated curves and experimental data, in spite of the theoretical defects in the basic assumption.

In its simplified form, which assumes the formation of the monohydrate only, the isotherm is:

$$\underline{Mr} / 1800 = [\alpha \underline{h} / (1 - \alpha \underline{h})] + [\alpha\beta \underline{h} / (1 + \alpha\beta \underline{h})]$$

where

$\underline{M}$ = "molecular weight" of the operative polymer unit

$\underline{r}$ = moisture regain, grams per 100 grams of dry sample

$\underline{h}$ = percentage relative humidity, and α and β are constants.

In accordance with the suggestion of Hailwood and Horrobin, this equation was reduced to the form

$$\underline{A} + \underline{Bh} - \underline{Ch}^2 = \underline{h} / \underline{r}$$

by the substitution of

$$\underline{A} = \underline{M} \,/\, [1800\ \alpha\ (\beta + 1)]$$

$$\underline{B} = \underline{M}\ (\beta - 1) \,/\, [1800\ (\beta + 1)], \text{ and}$$

$$\underline{C} = \underline{M}\ \alpha\beta \,/\, [1800\ (\beta + 1)].$$

$\underline{A}$, $\underline{B}$, and $\underline{C}$ were calculated by simultaneous equations formed from the three moisture regains determined experimentally. $\underline{M}$ was calculated from the relationship

$$\underline{M}^2 = (3600)^2\ \underline{AC} + (1800)^2\ \underline{B}^2$$

Since $\underline{M}$ is the molecular weight corresponding to one hydroxyl group taking part in the adsorption, and the actual molecular weight per hydroxyl for cellulose is 162, the inaccessible fraction is given by $(\underline{M}-162) \,/\, \underline{M}$.

Adsorption data and the calculated values of $\underline{M}$ and the inaccessible fractions are given in Table V.

TABLE V

ADSORPTION AND ACCESSIBILITY DATA

Sample	Relative Humidity, %	Moisture Regain $\underline{r}_1$	$\underline{r}_2$	Av. $\underline{r}$	$\underline{M}$	Percentage Inaccessible
J	11.1	3.40	3.37	3.39		
	32.8	5.50	5.80	5.65		
	64.8	9.73	9.65	9.69	383	57.7
K	11.1	2.00	2.05	2.03		
	32.9	3.98	3.94	3.96		
	64.8	6.99	6.97	6.98	476	66.0
L	11.1	4.85	4.75	4.80		
	32.9	8.20	7.87	8.04		
	64.8	14.90	14.69	14.79	284	43.0
M	11.1	6.49	6.50	6.50		
	32.9	10.43	10.19	10.31		
	64.8	15.39	15.58	15.48	193	16.1
N	11.1	3.34	3.22	3.28		
	32.9	5.70	5.44	5.57		
	64.8	9.48	9.52	9.50	382	57.6
P	11.1	3.08	3.02	3.05		
	32.9	5.49	5.71	5.60		
	64.8	9.76	9.52	9.64	353	54.1

PRELIMINARY WORK FOR DIELECTRIC CONSTANT MEASUREMENTS

PREPARATION OF REFERENCE LIQUIDS

Benzene and ethylene chloride were used as reference liquids, since they had been found satisfactory in the work of DeLuca, Campbell, and Maass (37). Thiophene-free benzene was distilled over phosphorus pentoxide to insure dryness, and was stored over sodium until ready for use.

Several methods were tried for purifying ethylene chloride to a point such that its conductivity would be low enough to make the use of the Schering bridge possible. Resistance, as measured by a vacuum tube ohmmeter, was used

as the criterion of purity. Copper electrodes mounted permanently in a Teflon base were used as the conductivity cell. The resistance as measured by this method was approximately 10 times that obtained in the test capacitor. The original C.P. ethylene chloride had a resistance of 5 to 6 megohms.

(1) Distillation of Ethylene Chloride Over Phosphorus Pentoxide

An all-glass distillation setup with a fractionating column was used for this work. One-half pound of phosphorus pentoxide was used for each liter of ethylene chloride and only the middle boiling fraction was collected. The resistance of the resulting ethylene chloride was 18 megohms.

(2) Phosphorus Pentoxide Distillation Followed by Sodium Hydroxide Distillation

The same distillation setup as in (1) was used; the system was closed except for a calcium chloride drying tube attached to the receiver. The resistance from the phosphorus pentoxide distillation was 25 megohms. The resistance from the sodium hydroxide distillation was 5 to 6 megohms.

(3) Silica Gel

The ethylene chloride was mixed with fresh silica gel and filtered. The resulting ethylene chloride had a resistance of 70 megohms.

(4) Distillation Over Phosphorus Pentoxide in Absence of Light

The same distillation apparatus used in (2) was used except that the entire system was painted with black paint to exclude light. The distillate had a resistance of 50 megohms. Half of this distillate was stored over silica gel and one-half with no desiccant. After 60 hours the resistance of the ethylene chloride stored over silica gel was 45 megohms. The normally stored product had a resistance of 20 megohms.

(5) Distillation Over Calcium Oxide

The C.P. ethylene chloride was allowed to stand over freshly burned calcium oxide for two days. The mixture was refluxed for one hour and distilled. The resistance of the distillate was 8 megohms.

(6) Vacuum Distillation Over Phosphorus Pentoxide

A very slow distillation over phosphorus pentoxide was carried out at 6.25 inches of mercury. The distillate had a resistance of 50 megohms.

(7) Vacuum Distillation Over Phosphorus Pentoxide Followed by Sodium Hydroxide Treatment

The distillate from (6) was shaken with sodium hydroxide pellets for 15 minutes. The resistance of the decanted ethylene chloride was 1000 megohms.

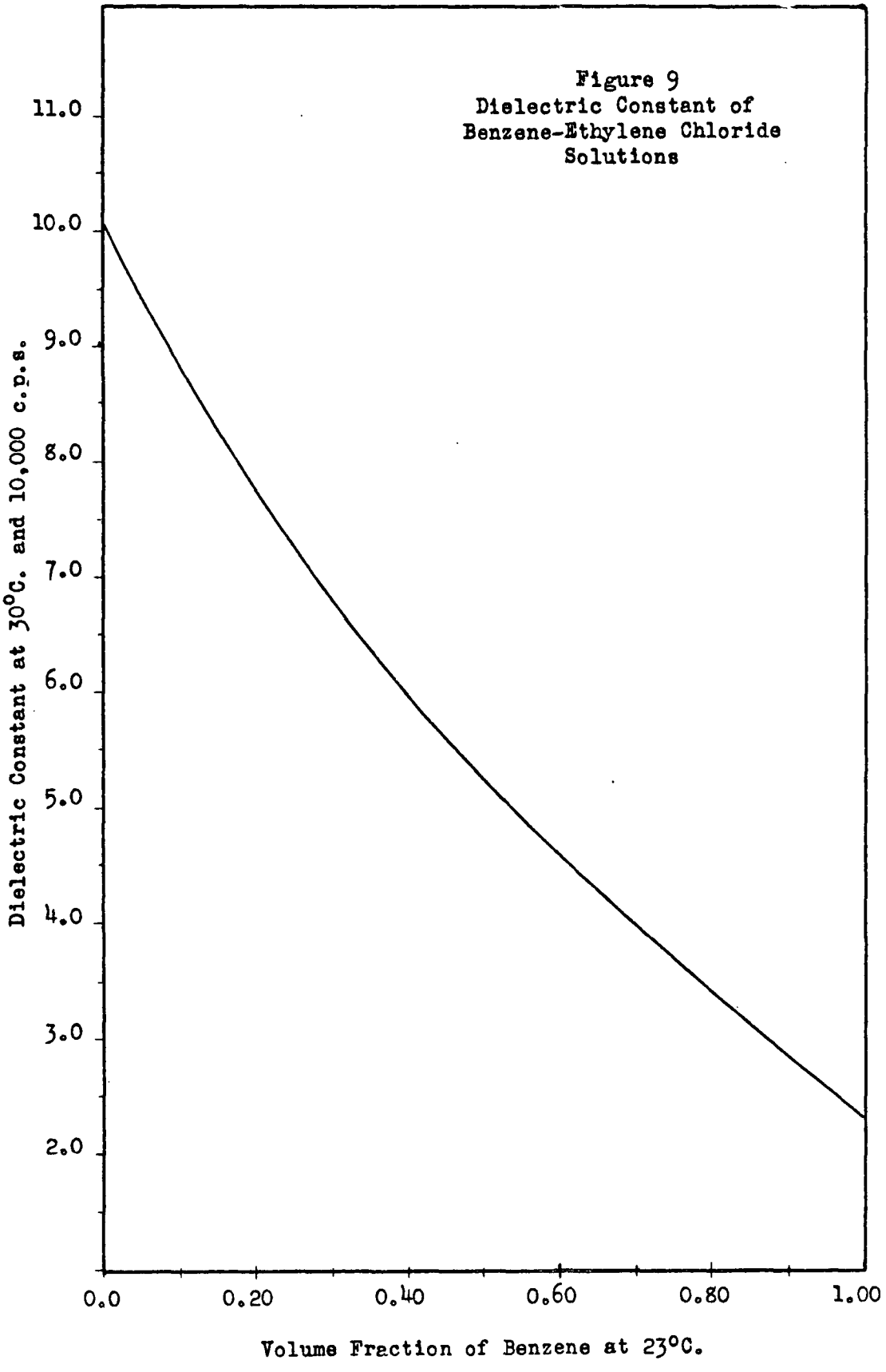
(8) Distillation Over Phosphorus Pentoxide With Storage Over Potassium Hydroxide

Potassium hydroxide sticks were placed in the freshly distilled ethylene chloride. This type of storage kept the resistance of the distillate at about 90 megohms, which was found to be satisfactory when the modifications of the bridge were made.

Mixtures of ethylene chloride and benzene were prepared as needed and were redistilled over phosphoric anhydride after use. The dielectric constant at 30°C. is shown as a function of volume fraction at 23°C. in Figure 9. Mixtures were made up by volume fractions or, in the case of the redistilled mixtures, by specific gravity. At 30°C. the dielectric constant of benzene is 2.274 and that of ethylene chloride is 10.08 (55).

The liquid calibration curve is useful only for approximations because the composition of the liquid changes slightly when it is subjected to the

Figure 9
Dielectric Constant of
Benzene-Ethylene Chloride
Solutions



vacuum filling operation. The extent of this change is dependent upon the extent of evacuation and the volume of the evacuated space. When the vacuum pump is kept in operation during the filling operation, as was the normal procedure, the change in composition could result in a change in dielectric constant of several hundredths. The change could also be detected by measuring the specific gravity of the liquid in the cold traps and comparing it with that of the liquid in the condenser housing. It was to overcome this difficulty that the reference capacitor, C_r, was installed.

TIME REQUIRED FOR TEMPERATURE EQUILIBRIUM

The test condenser housing was surrounded by a water bath, the temperature of which was controlled to $\pm$ 0.05°C. Temperature changes within the test capacitor occurred much too rapidly to follow them by capacitance change measurements; however, constant capacitance, within the accuracy of the system, was attained less than one hour after filling.

When the temperature dependence of the dielectric constant was utilized, a more accurate measurement of temperature and equilibrium time was desirable. This was obtained by inserting a thermocouple into the condenser housing from the cold trap at X, (Figure 7). Temperature equilibrium was attained in fifteen to thirty minutes depending upon the degree of temperature change involved.

CALIBRATION OF THE PRECISION CAPACITOR FOR INTERNAL CONSISTENCY

The General Radio precision capacitor, C_2 in Figure 3, has two ranges, the high range of 100 to 1100 mmfd., and the low range of 25 to 110 mmfd. The guaranteed accuracy of the high range is $\pm$ 1 mmfd. and that of the low range is $\pm$ 0.2 mmfd. With suitable calibration by the manufacturer, the accuracy of both ranges can be increased somewhat. (General Radio Company, Catalogue M.)

The vacuum capacitance of each of the experimental capacitors, C_p and C_r, was determined on the low range of the precision capacitor as the average of five measurements. Using these capacitance values, the high range of the precision capacitor was calibrated for internal consistency by stepwise measurements of the capacity of each of the experimental capacitors. This method of calibration is described in detail by Smyth (56). The two calibration curves obtained (one for each of the experimental capacitors) were drawn and the mean of these two curves was used for the correction of all capacitance readings made on the precision capacitor. In the range of 300 to 870 mmfd. a precision of $\pm$ 0.1 mmfd. in capacitance difference could be obtained by the use of this calibration curve.

CALIBRATION OF EXPERIMENTAL CONDENSERS

The total vacuum capacitance of the test condenser, or the reference condenser, referred to in the previous section, includes a small capacitance which is not affected by the dielectric constant of the surrounding medium. This capacitance, which is designated $\underline{C}_L$, arises from the small portion of the condenser area which is taken up by the glass spacers and from the capacitance between the condenser leads. The latter capacitance is probably very small in the equipment used in the present work.

If $\underline{C}_c$ represents the portion of the total capacitance which varies in direct proportion to the dielectric constant of the surrounding medium, and $\underline{C}_T$ is the capacitance measured with the capacitance bridge,

$$\underline{C}_T = \underline{C}_c \varepsilon + \underline{C}_L$$

where ε is the dielectric constant of the medium. When $\underline{C}_T$ is determined for two dielectrics of known dielectric constant, $\underline{C}_c$ and $\underline{C}_L$ can be calculated.

The dielectric constant of a material in either capacitor is then

$$\varepsilon = (\underline{C}_T - \underline{C}_L) / \underline{C}_c$$

Normally the vacuum capacitance and the capacitance in benzene were used to obtain the two equations necessary to calculate $\underline{C}_L$ and $\underline{C}_c$. Additional values of ε could be obtained by changing the temperature of the benzene. This calibration was made for both C_p and C_r whenever adjustments were made to the test condenser system. In addition to this calibration procedure, the dielectric constant of another liquid was occasionally determined with each of the experimental condensers. The values obtained agreed within $\pm$ 0.002.

The corrected capacitance, $\underline{C}_c$, of each of the experimental condensers was approximately 42 mmfd. Capacitance changes brought about by adjusting the retaining nuts on these condensers were seldom as great at 0.1 mmfd.

PRELIMINARY DIELECTRIC CONSTANT MEASUREMENTS

In the initial stages of the investigation of the effects of bonding upon the dielectric constant of cellulose, a number of measurements were made on bonded (dried from water) and unbonded (dried by solvent replacement) linters. While these measurements were later found to be in error they were useful from the standpoint of developing experimental procedures. The capacitor used for these experiments was not as rigid as the capacitor used in work on bonding and crystallinity studies and, as a result, the precision of the measurements was too poor for any but qualitative interpretation.

Water-formed sheets, vacuum dried while in place in the capacitor, exhibited dielectric constants ranging from 4.0 to 5.4. If these sheets were removed from the capacitor, conditioned at room humidities (30 to 50% relative humidity), and again placed in the test capacitor, dried and measured, their dielectric constant apparently increased to about 5.7. This discrepancy led to an investigation of the effect of drying conditions upon dielectric constant, which is detailed in a later section. The apparent difference was later found to be entirely due to the deformation of the test capacitor caused by the curling of the sample pad in vacuum drying. After exposure to 50% relative humidity the curling of the sample pad no longer caused a deformation of the capacitor, nor did deformation occur upon subsequent drying in vacuo.

Sheets dried from benzene did not present this curling problem, and furthermore, they consistently gave higher dielectric constants than water-dried sheets, indicating a possible effect of bonding upon dielectric constant. The precision of dielectric constant measurements made on solvent replacement-dried cellulose was somewhat better than that obtained with water-dried cellulose. Other advantages to be gained by working with solvent-dried cellulose are the minimizing of density variations and the rapidity of drying. All of these factors entered into the selection of the solvent-drying method of sample preparation for the crystallinity studies.

DIELECTRIC CONSTANT MEASUREMENTS

EXPERIMENTAL PROCEDURE

The cellulose pad, cut to the proper size and shape, was inserted into the lower test capacitor through the open side. The condenser housing was

reassembled and the external leads attached. The assembled cell was slipped into place in the vacuum system. Dewar flasks, containing dry ice and acetone, were placed over the traps and the system was flushed with dry air entering at A and leaving at F (Figure 7). A storage bottle containing 550 milliliters of the reference liquid was placed in position 6. With dried air entering at C and leaving at D under reduced pressure, stopcock G opened to allow the liquid to fill the delivery tube, at which time G was closed. The drying operation was carried out at about 10 microns pressure, overnight for solvent replacement-dried samples, and for 36 hours for water-formed samples. The temperature of drying was 30°C. These drying times are approximately twice the time required to reach constant capacitance values for the cellulose-filled capacitor. When drying was complete the needle valves A' and C' were closed and G was opened until approximately 500 milliliters of liquid was run in. Stopcock G was then closed and the vacuum pump lines closed off at D and F. At this point the capacitor cell was completely filled with liquid. A and C were opened and air was cautiously admitted to the system by means of the needle valves A and C. The flow rate of the air was controlled at both sides so that the liquid remained in the cell. When the pressure in the system reached atmospheric pressure, A and C were closed. The constant temperature bath was brought to a temperature slightly above room temperature and sufficient time allowed for temperature equilibrium. Capacitance readings are usually made at 25, 27, and 30°C.

When capacitance measurements were completed, the system was drained and evacuated. Evacuation for four hours was sufficient to remove the residual liquid from the system, at which time the next reference liquid was admitted.

Two capacitance measurements were made at each temperature on each of the capacitors. The capacitance corrections for the precision capacitor were made on all readings and the average of the two corrected capacitances was used for the calculation of the dielectric constant. The temperature was measured to the closest 0.1°C. Capacitance measurements made for both ascending and descending temperature variation lie on the same curve, within experimental error.

Temperature Dependence of the Dielectric Constant of Cellulose

One advantage to the use of the temperature variation method of determining dielectric constant is that a good estimate of the dielectric constant can be made with the use of only one liquid. When this is done, the second liquid may be selected such that its dielectric constant will be adequately close to that of the cellulose. Before considering the actual value of the temperature dependence of the dielectric constant of cellulose, however, an estimate of the reliability of the method should be made.

When the intersection of two nearly parallel lines, such as those in Figure 2, is determined, considerable error may be introduced by a slight displacement of the lines or a slight change in their slopes. The difference in the position and slope of these lines is determined by the difference between the dielectric constant of the liquid and that of the cellulose, the amount of cellulose present, and the temperature dependence of the dielectric constant of the liquid. Because of these factors, no fixed value for the maximum error in the intersection can be given. Generally speaking, however, a maximum error of 0.002 in the dielectric constant of the liquid and the liquid-cellulose mixtures can produce a maximum error

of 0.05 in the intersection for the temperature ranges used in this work. Since one determination is always made with the intersection within one degree of 30°C., the maximum error expected in the dielectric constant values is ± 0.05.

Because of this source of error, considerable variation in the slopes of the cellulose dielectric constant vs. temperature curve can be expected. The actual variation may be seen in Table VI. Where the intersection at 30°C. was obtained with only one liquid, no slope value can be given.

TABLE VI

TEMPERATURE DEPENDENCE OF THE DIELECTRIC CONSTANT OF CELLULOSE

Sample	$\frac{d\varepsilon_c}{dt}(°C.)^{-1}$
A-3	0.0156
B	0.0098
D	0.0106
J-1	0.0097
J-2	0.0092
K-2	0.0126
L-1	0.0087
	Av. 0.0109

The value for $\frac{d\varepsilon_c}{dt}$ used for predicting the dielectric constant of cellulose at 30°C. from a value at some other temperature was 0.01 per degree Centigrade. Since the temperature ranges involved were usually quite small, this method of estimation was quite satisfactory.

EFFECT OF DRYING CONDITIONS ON THE DIELECTRIC CONSTANT OF WATER-FORMED SAMPLES

In order to determine the effects of bonding upon the dielectric constant of cellulose, the dielectric constant of samples dried from water was compared to the dielectric constant of samples dried by solvent replacement. The highly beaten cotton linters stock was used in these experiments. Because of the effect of moisture upon vacuum-dried sheets, described in a previous section, a study of the effect of initial drying conditions upon dielectric constant is included.

All sheets were dried while clamped between drying rings. Drying time for all samples, except those vacuum dried, was two weeks. Vacuum-dried samples were immersed in benzene to prevent exposure to the atmosphere when the samples were placed in the capacitor. Table VII gives the drying conditions and the resultant dielectric constants of various samples.

TABLE VII

EFFECT OF DRYING CONDITIONS ON DIELECTRIC CONSTANT

Sample	Drying Conditions	Dielectric Constant
B	47°F. over P_2O_5	5.70
C	73°F. over P_2O_5	5.69
D	73°F. at 50% R.H.	5.70
E	47°F. at 50% R.H.	5.72
G	Vacuum dried	5.8
E'	Vacuum dried	5.73

Measurements made on three additional samples, dried at 73°F. at 50% relative humidity without restraint, gave values of 5.75, 5.82, and 5.81 for an average of 5.79 (Sample A).

In the range investigated no significant change in the dielectric constant of cellulose was produced by variation of the initial drying conditions. The dielectric constant of solvent replacement-dried cotton linters is given in the following section as 5.86. The average dielectric constant of cotton linters dried from water is 5.72 (average of A, B, C, D, and E). The lowering of dielectric constant caused by inter- and intrafiber bonding in linters appears to be of the order of 0.1. In light of the wide variation obtained for dielectric constant values for linters dried from water, no fixed value can be given for this difference.

Effect of Bonding on Dielectric Constant

In the previous section the lowering of the dielectric constant by inter- and intrafiber bonding was given as approximately 0.1. This figure was based on a dielectric constant of 5.86 for solvent replacement-dried cotton linters and 5.72 for water-dried linters. The density of water-dried linters has been found to be 1.53 g./cc. and that of solvent-dried cellulose 1.58. These density figures are a measure of the extent to which the reference liquids can penetrate the cellulose in the dielectric constant determination.

If the Clausius-Mosotti equation is valid for the small density differences in this density range, the dielectric constants of the two samples can be compared at equal densities. At the density of the unbonded cotton linters (1.58 g./cc.) the dielectric constant of the bonded

linters would be 5.94, approximately 0.1 higher than that of unbonded linters. Since bonding would be expected to tie up hydroxyl groups in much the same way as crystallization, such a result is unexpected. This result might be due to a failure of the Clausius-Mosotti equation at high densities. A more reasonable explanation, however, is that the two values are not significantly different and that the effects of bonding, per se, upon dielectric constant are too slight to be detected. A third possibility is that more moisture was retained by the water-formed sheet than by the solvent-dried sheet under the particular drying conditions used. However, in view of the small influence initially adsorbed water has upon the dielectric constant of cellulose, this explanation does not appear reasonable.

THE RELATIONSHIP BETWEEN DIELECTRIC CONSTANT AND ACCESSIBILITY

Cellulose pads for the dielectric constant determinations in this study were made from the benzene suspension when required. In order to prevent adsorption of atmospheric moisture by the sample, the latter was kept saturated with benzene from the time of formation until the vacuum drying was started. All dielectric constant determinations were made in duplicate.

Table VIII lists the dielectric constant values obtained at the various accessibilities studied.

TABLE VIII

RELATIONSHIP BETWEEN DIELECTRIC CONSTANT AND ACCESSIBILITY

Sample	Accessibility, %	Dielectric Constant 1	2	Av.
J	42.3	5.86	5.86	5.86
K	34.0	5.46	5.52	5.49
L	57.0	6.54	6.59	6.56
M	83.9	7.87	7.86	7.86
N	42.4	5.83	5.89	5.86
P	45.9	6.15	--	6.15

Figure 10 shows the relationship between dielectric constant and accessibility in graphical form. The straight line is a least squares regression line, $\varepsilon_c - 6.30 = 0.0474\ (\underline{A}-50.9)$ where $\underline{A}$ is accessibility. The correlation coefficient is 0.998.

This relationship clearly shows the importance of the freedom of the free hydroxyl groups and of portions of the cellulose molecules in determining the dielectric constant of cellulose. In crystalline portions of the cellulose structure such motion is restricted, and the polarizations would consist, primarily, of electronic and atomic polarization.

The dielectric constant of cellulose might be thought of as the dielectric constant of a complex two-component system, one component being the inaccessible fraction and the second component the accessible fraction. The assignment of definite dielectric constants to the two fractions is probably not entirely accurate. The dielectric constant of crystalline cellulose will depend to some extent upon the size of the crystallite, or, more

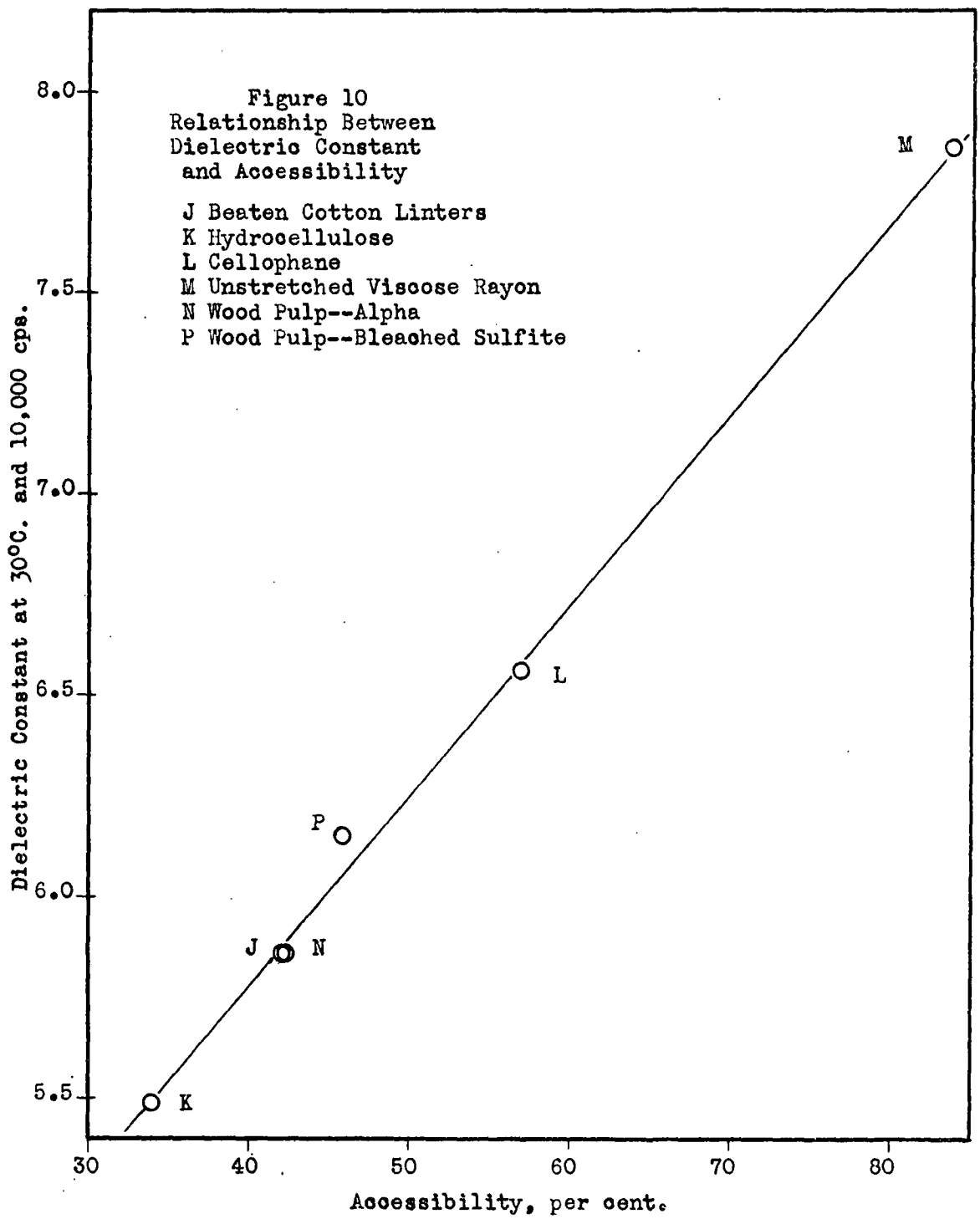


Figure 10
Relationship Between
Dielectric Constant
and Accessibility
J Beaten Cotton Linters
K Hydrocellulose
L Cellophane
M Unstretched Viscose Rayon
N Wood Pulp--Alpha
P Wood Pulp--Bleached Sulfite
Dielectric Constant at 30°C. and 10,000 cps.
8.0
7.5
7.0
6.5
6.0
5.5
30
40
50
60
70
80
Accessibility, per cent.
K
J
N
P
L
M

properly, upon the surface area to volume ratio of the crystallite. This would be expected since the surface molecules will have some polar groups not bound in the crystal lattice and free to rotate to a limited extent. Therefore, the dielectric constant of a very small crystallite should be somewhat larger than that of a larger crystallite. When the entire cellulose structure is considered, however, the average dielectric constant of the crystalline fraction might be relatively constant, even for entirely different celluloses. A second factor to be considered is the difference in the unit cells of native and regenerated cellulose; however, Calkins (30) found no significant change in dielectric constant brought about by a change of the unit cell.

The dielectric constant of amorphous cellulose would appear to be influenced considerably by the proximity and configuration of adjacent molecules. The dielectric constant of this substance would vary from that of the transitional, or mesomorphous, region to that of the completely amorphous region. The actual range of dielectric constants involved, however, need not be great. The polarizations expected in the amorphous regions, in addition to electronic and atomic polarizations, are those caused by movement of polar groups. In the transitional region of amorphous cellulose all of these polarizations continue to be possible. The molecular and dipolar polarizations may be influenced somewhat by the proximity of the adjacent molecules, but the rigid secondary valence restrictions are not present. Therefore the dielectric constant of mesomorphous cellulose may be very nearly equal to that of amorphous cellulose. Again, as in the case of crystalline cellulose, the average dielectric constant of the amorphous regions should be considered. Such a value should be quite constant even among celluloses of quite different crystalline-amorphous ratios.

Some factors which might complicate the concept of a two-component system are the presence of interfacial polarizations and possible anisotropy. There is no evidence, however, that either of these factors create any serious discrepancies.

If this two-component concept is a valid one and the dielectric constants of the two components can be represented by two average values, the data can be represented by an equation of the form

$$\varepsilon_c = \underline{V}_a\varepsilon_a + \underline{V}_i\varepsilon_i$$

where ε_c = the mean dielectric constant of the cellulose sample.

$\underline{V}_a$ = the volume fraction of accessible cellulose.

ε_a = the dielectric constant of accessible cellulose.

ε_i = the dielectric constant of inaccessible cellulose.

$\underline{V}_i$ = the volume fraction of inaccessible cellulose.

This equation, of course, represents a straight-line relationship. Because of the limited range of accessibilities studied, some relationship other than that of a straight line may be possible. Table IX gives three possible equations which fit the data quite well. The calculated values of ε_a, ε_i, and the correlation coefficient of the relationships are also given. The correlation coefficients are those existing between the left-hand member of the equation and the accessibility. Equation (1) is the linear equation, shown in Figure 10, written to show how the dielectric constant of cellulose could be considered as the average dielectric constant of the accessible and inaccessible portions suitably weighted with respect to volume fraction present. Equation (2) expresses the dielectric constant of cellulose as the

dielectric constant of two different dielectrics in series arrangement. Equation (3) is a modified form of Equation (1), where polarization, rather than dielectric constant, is averaged (38).

TABLE IX

EQUATIONS RELATING DIELECTRIC CONSTANT AND ACCESSIBILITY

$$\varepsilon_c = \underline{v}_a\varepsilon_a + \underline{v}_i\varepsilon_i \qquad (1)$$

$\varepsilon_a = 8.62$ $\varepsilon_i = 3.88$ Correlation coefficient 0.998

$$1/\varepsilon_c = (\underline{v}_a/\varepsilon_a) + (\underline{v}_i/\varepsilon_i) \qquad (2)$$

$\varepsilon a = 9.24$ $\varepsilon_i = 4.64$ Correlation coefficient 0.993

$$(\varepsilon_c-1) / (\varepsilon_c+2) = [\underline{v}_a (\varepsilon_a-1) / (\varepsilon_a+2)] + [\underline{v}_i (\varepsilon_i-1) / (\varepsilon_i+2)] \qquad (3)$$

$\varepsilon_a = 9.05$ $\varepsilon_i = 4.51$ Correlation coefficient 0.996

As can be seen from Table IX there is little basis for selecting any one of these equations in preference to the others. The latter two curves are represented graphically in Figures 11 and 12. From an entirely subjective point of view the data appear best represented by the straight-line relationship. Little more can be said, however, than that the dielectric constant of inaccessible cellulose appears to be about four and the dielectric constant of accessible cellulose about nine.

Another possible interpretation of the data, besides the two-component concept, is that the dielectric constant of amorphous cellulose is capable of

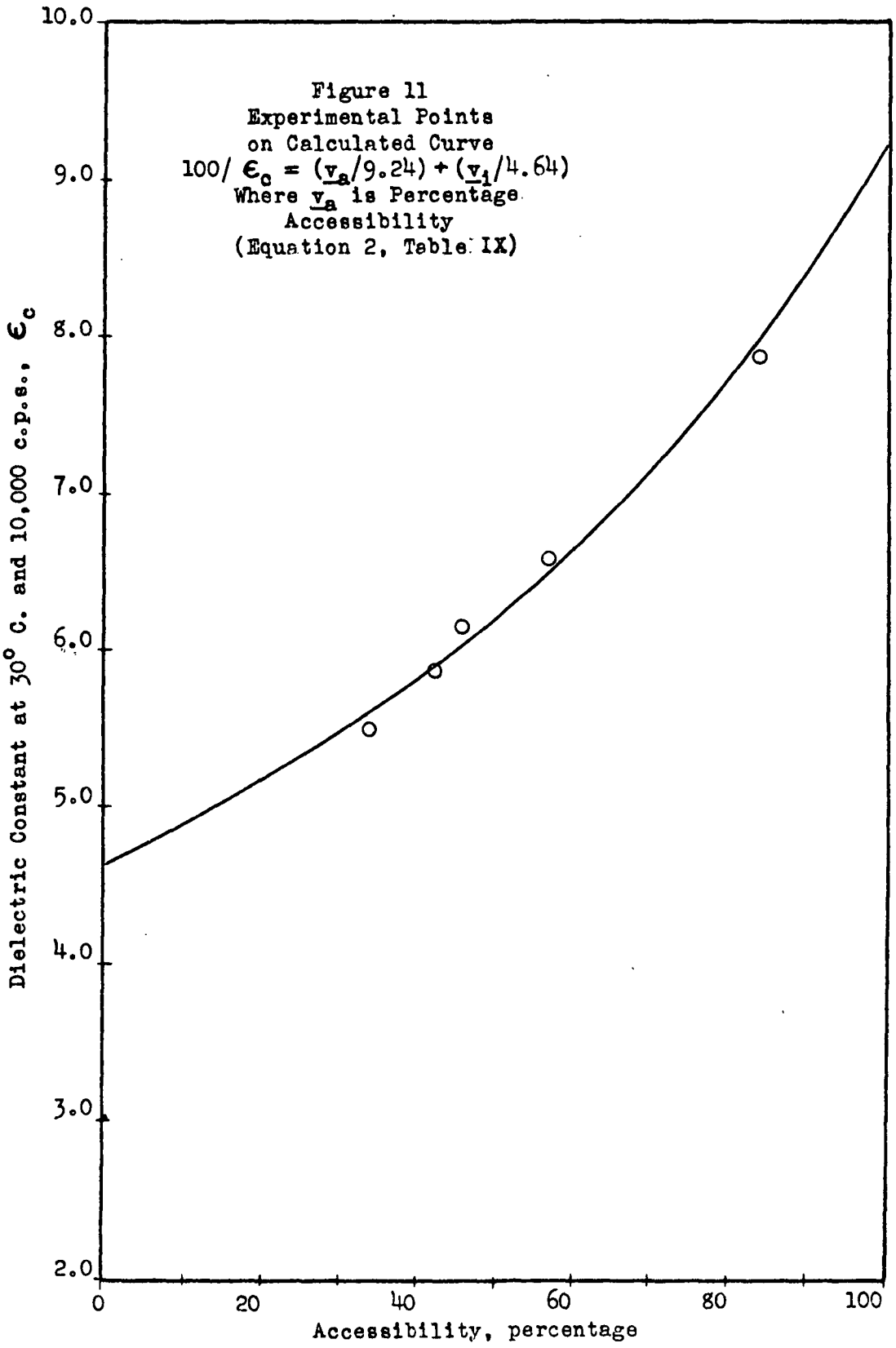


Figure 11
Experimental Points
on Calculated Curve
100/ ϵ_c = (v_a/9.24) + (v_i/4.64)
Where v_a is Percentage
Accessibility
(Equation 2, Table IX)
Dielectric Constant at 30° C. and 10,000 c.p.s., ϵ_c
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
0
20
40
60
80
100
Accessibility, percentage

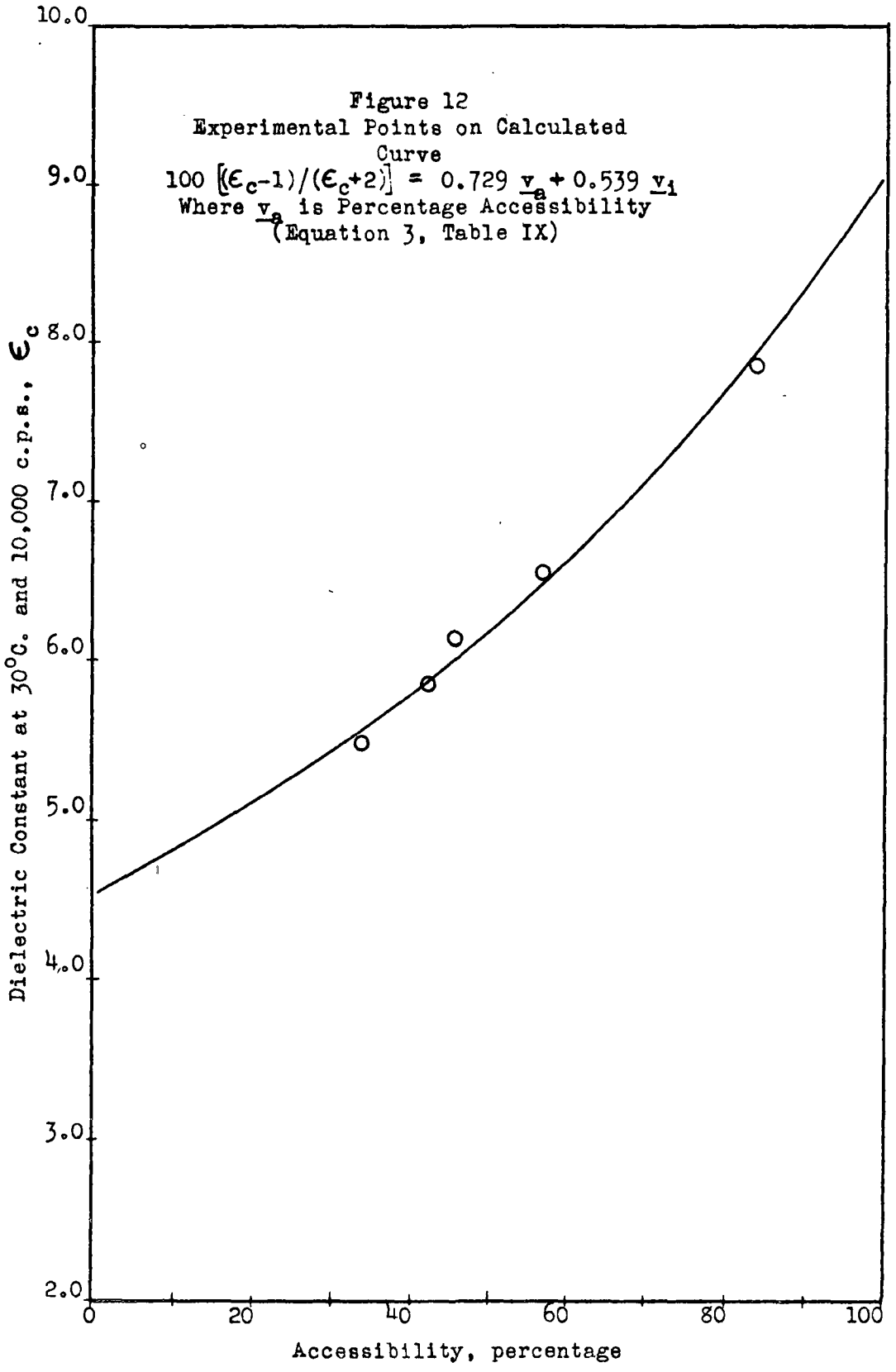


Figure 12
Experimental Points on Calculated Curve
$100\left[(\epsilon_c-1)/(\epsilon_c+2)\right] = 0.729\ \underline{v}_a + 0.539\ \underline{v}_i$
Where $\underline{v}_a$ is Percentage Accessibility
(Equation 3, Table IX)

varying over quite a large range, i.e., from a value essentially equal to that of crystalline cellulose with a high surface to volume ratio to that of an isolated cellulose molecule. The crystallite size could also be a critical factor in the dielectric constant of crystalline cellulose. A decrease in crystallinity would then result in a greater chance for the amorphous chains to achieve random disorder and isolation, hence a higher dielectric constant. The same decrease in crystallinity might result in a decrease in crystallite size, which could cause as increase in the dielectric constant of the crystalline portion of the cellulose. The wide range in dielectric constant for either crystalline or amorphous cellulose which might be possible in such a system as this would, of course, have practical limits. Under such limits the representation of the system as a two-component system could be quite accurate, although it should be recognized that the dielectric constant of cellulose could be strongly influenced by the size and distance of separation of individual crystallites.

This latter concept differs from the two-component concept primarily in the relative importance attached to the restrictive influence of nearby molecules upon the polarization of a given molecule. If this influence is small, when compared with the restriction of secondary valence forces, the two-component concept should offer the best representation of the system.

SUMMARY AND CONCLUSIONS

A test capacitor system has been built and existing equipment modified to make possible the measurement of the dielectric constant of cellulose at, or near, its ultimate density by immersion in liquids of varying dielectric constant.

Such measurements were made at a temperature of 30°C. and a frequency of 10,000 cycles per second on six different celluloses. These celluloses were purified cotton linters, cellophane, hydrocellulose, two wood pulps, and a high accessibility regenerated viscose.

A slight decrease in the dielectric constant of cellulose, brought about by bonding, was attributed to the lower density of the bonded sheet as compared to that of the unbonded. This effect was eliminated by drying the cellulose by solvent replacement. No effect of bonding, per se, upon dielectric constant was apparent.

The dielectric constant of cellulose was found to be profoundly influenced by the amount of inaccessible material present, as calculated from water-vapor accessibilities. The range of accessibilities studied was approximately from 35 to 85%. The relationship with dielectric constant in this range was very nearly linear. A two-component system, consisting of accessible and inaccessible cellulose, was hypothesized. The dielectric constants suggested by this hypothesis are approximately four for crystalline cellulose to nine for amorphous cellulose. The experimental data are very well represented by such a concept. More extensive data must be obtained, however, before the quantitative value of the relationship can be determined.

The dielectric constant of cellophane, contrary to the experience of Calkins and Verseput, was found to fit the relationship quite well. A possible explanation of this is that the Clausius-Mosotti relationship may be invalid for density differences of the magnitude existing between the density of cellophane and that of fibrous cellulose sheets. A second indication of the invalidity of this relationship over wide density ranges is suggested by the maximum value of 7.8 obtained for the dielectric constant of a regenerated cellulose. Verseput calculated, by means of the Clausius-Mosotti equation, that the dielectric constant of such a cellulose could be as high as from ten to twelve.

The possibility of using dielectric constant measurements as a measure of crystallinity in cellulose appears to be very promising. The limited experimental data can be represented by a linear relationship with a maximum error of 0.1 in the dielectric constant. However, further study, involving other physical measurements of crystallinity, such as x-ray diffraction measurements, appears desirable.

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